Designing $\pi$–conjugated polymers with light emission in the infrared

S. Mazumdar,\textsuperscript{1} S. Dallakyan,\textsuperscript{1} and M. Chandross\textsuperscript{2}

\textsuperscript{1} Department of Physics, University of Arizona Tucson, AZ 85721
\textsuperscript{2} Sandia National Laboratories, Albuquerque, NM 87185-1411

There is currently a great need for solid state lasers that emit in the infrared. Whether or not conjugated polymers that emit in the IR can be synthesized is an interesting theoretical challenge. We show that emission in the IR can be achieved in designer polymers in which the effective Coulomb correlation is smaller than that in existing systems. We also show that the structural requirement for having small effective Coulomb correlations is that there exist transverse $\pi$–conjugation over a few bonds in addition to longitudinal conjugation with large conjugation lengths.

PACS numbers:

All light emitting $\pi$–conjugated polymers to date emit in the visible or UV. Telecommunications use infrared radiation, so lasing at these wavelengths is desirable. Within conventional theories of light emission from $\pi$-conjugated polymers, light emission in the IR from undoped $\pi$-conjugated polymers would be impossible. In this paper we point out the structural modifications that can lead to emission in the IR.

Linear polyenes and trans-polyacetylene (t-PA) are weakly emissive, because the lowest two-photon state, the $2A_g$, occurs below the optical $1B_u$. The optically pumped $1B_u$ decays to the $2A_g$ in ultrafast times, and radiative transition from the $2A_g$ to the ground state $1A_g$ is forbidden. Strong photoluminescence (PL) in systems like PPV and PPP implies $E(2A_g) > E(1B_u)$ (where $E(\ldots)$ is the energy of the state). This reversed excited state ordering can be understood by enhanced bond alternation within the effective linear chain model for PPV, PPP, etc.\textsuperscript{1} Since enhanced bond alternation necessarily increases $E(1B_u)$, it appears that strong PL should be limited to systems with optical gaps larger than that of t-PA.

Our goal is to demonstrate theoretically that materials obtained by “site-substitution” of t-PA, in which the hydrogen atoms of t-PA are replaced with transverse conjugated groups of finite size will have small optical gaps and $E(2A_g) > E(1B_u)$. Systems obtained by such site-substitution consist of molecular units linked by a single longitudinal bond. With moderate e–e interactions, the ground state can be thought of as covalent (all atomic sites singly occupied). Optical excitation along the backbone chain involves inter-unit one-electron hops that generate C$^+$ and C$^-$ ions on different units. These charges are delocalized over entire molecular units, leading to considerable decrease in the effective on-site Coulomb interaction $U_{eff}$. Smaller $U_{eff}$ can now give smaller $E(1B_u)$ (relative to t-PA) and $E(2A_g) > E(1B_u)$.

Initial work along this direction by us was limited to poly-diphenylpolyacetylene (PDPA)\textsuperscript{2, 3}, in which the substituents are phenyl groups. PDPA\textsuperscript{2} emits in the visible or UV. Telecommunications use infrared. Whether or not conjugated polymers with conjugated sidegroups, the hypothetical polymer shown in Fig. 1, in which the substituents are ethylenes. This simple structure allows more insight than more complicated ones.

We consider linear polyenes as well as oligomers of the structure in Fig. 1 within the dimerized Hubbard Hamiltonian,

$$H = H_{1e} + H_{ee} \quad (1)$$

$$H_{1e} = - \sum_{\langle ij \rangle, \sigma} t_{ij} c_{i,\sigma}^\dagger c_{j,\sigma} \quad (2)$$

$$H_{ee} = U \sum_i n_{i,\uparrow} n_{i,\downarrow} \quad (3)$$

In the above, $H_{1e}$ describes one-electron nearest neighbor hops of electrons, and $H_{ee}$ is the electron-electron (e–e) interaction. We have used $t_{ij} = 2.2$ eV and 2.6 eV for single and double bonds, respectively. For both the unsubstituted and the substituted polyene we increase $U$ from zero (where $E(2A_g) > E(1B_u)$) and determine the critical $U_c$ at which $E(2A_g) < E(1B_u)$ occurs. A smaller $U_{eff}$ in the substituted polymer requires $U_c$(substituted) > $U_c$(unsubstituted).

The complete Hamiltonian is way beyond our reach for more than two units of the substituted polyene of Fig. 1.

\begin{figure}[h]
\centering
\includegraphics[width=0.2	extwidth]{fig1.png}
\caption{The hypothetical polymer investigated theoretically.}
\end{figure}
We therefor choose an appropriate minimal basis for the substituted system that allows many–body accurate calculations. Our approach is based on the exciton basis valence bond method [4], within which a linear polylene is considered as coupled ethylenic dimer units, and the polymer of Fig. 1 would be coupled hexatrienes. The basis considered is coupled ethylenic dimer units, and the valence bond method [5], within which a linear polyene

calculations. Our approach is based on the exciton basis

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other two-excitations with noncrossing singlet bonds, as is shown in Fig 3(c). The particular 2:1 superposition of these two VB diagrams is a triplet–triplet (TT) excitation, with two triplets on the two dimer units [5], as shown in Fig. 3(d). The diagrams in longer chains are similar to those shown in Fig. 3, – the only difference arises in the lengths of the interunit singlet bonds, which can be between nonnearest neighbor units in long chains. Furthermore, in the minimal basis (see Fig. 2), the same VB diagrams occur in the oligomer of Fig. 1 as in a linear polylene of the same length, the only difference arises from the fact that the expansions of the HOMO and the LUMO in the substituted polylene in terms of the atomic orbitals are different from that in the unsubstituted polylene, and hence the matrix elements of $H_{ex}$ and $H_{intr}$ are different.

We performed exact numerical calculations for unsubstituted and minimal basis substituted polyenes with N = 4, 6 and 8 backbone carbon atoms and quadruple-CI (QCI) calculations for the N = 10 system to determine $U_c$ for each of these systems. QCI gives practically exact energies for the lowest eigenstates at these chain lengths [1, 2]. In Fig. 4 we have plotted the excitation energies $E(1B_u)$ and $E(2A_g)$ [E(1A_g) = 0] for the N = 10 cases. Note that only is the $E(1B_u)$ for the substituted system smaller, $E(1B_u)$ in this case increases with $U$ much less rapidly than for the unsubstituted polylene. More importantly, the $U_c$ for the substituted system is larger than that for the unsubstituted polylene by more than 1 eV. The initial increase in $E(2A_g)$ for the substituted polylene is real and has been seen previously in calculations for long polyenes [4], where it was found that the smaller the $2A_g - 1B_u$ gap at $U = 0$, the more the tendency to initial increase of $E(2A_g)$. This particular energy gap is obviously smaller in the substituted polylene.

Fig. 5 shows the difference $\Delta U_c$ between the $U_c$ val-
ues for the substituted and the unsubstituted polyenes against $1/N$. $\Delta U_c$ increases modestly between $N = 4$ and 8, but then appears to saturate. The tendency to saturation in $\Delta U_c$ is an indirect signature of the accuracy of the minimal basis calculations: since the number of levels being ignored in the incomplete CI calculations for the substituted cases increases with $N$, had the larger $U_c$ for the substituted polyenes been a consequence of incomplete CI, $\Delta U_c$ would have increased continuously with increasing $N$.

In addition to calculations of energies, we have also done wavefunction analysis of the $1B_u$ and the $2A_g$ to verify that the effective on-site Coulomb correlation is smaller in the substituted polyene. While the $1B_u$ wavefunctions are very similar at fixed $U$, the $2A_g$ wavefunctions of the unsubstituted and the substituted polyenes are substantially different. For the specific case of $U = 6$ eV in Fig. 4, the $2A_g$ of the polyene is composed almost entirely of TT two-excitations (see Fig. 3(d)), while the largest contributions to the $2A_g$ of the substituted polyene come from the CT one-excitations (see Figs. 3(a) and (b)). Indeed, the $2A_g$ of the substituted polyene is very similar to the $2A_g$ of the unsubstituted polyene with large bond-alternation, for which also $E(2A_g) > E(1B_u)$. We thus see that at least within the minimal basis, the substituted polyene has a substantially smaller $U_{\text{eff}}$.

We now argue that complete CI, viz., going beyond the minimal basis of Fig. 2 will not alter the basic result that there exists a range of $U$ over which the $E(2A_g) > E(1B_u)$ in the substituted polyene but $E(2A_g) < E(1B_u)$ in the unsubstituted material. CI between the minimal basis TT exciton basis VB diagrams that have been retained in our calculations and higher energy TT diagrams that have been ignored can potentially lower the $2A_g$ energy in the substituted polyene. The higher energy TT diagrams are of two kinds, (i) TT excitations involving a single molecular unit, and (ii) those involving two units. We first discuss the role of type (i) TT excitations. In Fig. 6(a) - (d) we have shown four of the basis functions that dominate the molecular $2A_g$ state [10] (here the lowest three MOs are bonding, the higher three are antibonding). Diagram 6(a) is a superposition of one-excitations. Fig. 6(e) shows the CI between one of these diagrams and a minimal basis CT diagram. Such CI process can only raise the energy of the $2A_g$; hence we discuss this no further. Diagram 6(b) has already been included in our minimal basis calculations. This leaves diagrams 6(c) and (d). These can have CI with the minimal basis TT diagrams only through two applications of $H_{\text{inter}}^{1e}$, as shown explicitly in Fig. 6(f) and (g). Thus the TT diagrams 6(c) and (d) do indeed give the minimal basis TT diagrams, and this suggests that in principle CI processes such as these can lower $E(2A_g)$.

We point out, however, that the CI processes 6(f) and (g) are strictly local, i.e., molecular TT basis functions can be coupled only to minimal basis TT functions in which the two triplets occur on nearest neighbor units. Since in long chains there occur many more minimal ba-
sis TT diagrams with the triplets localized on distant units, it is clear that CI processes 6(f) and (g) become progressively unimportant with increasing chain length. Equally importantly, if the molecular unit is such that the molecular 2A\textsubscript{g} is above the molecular 1B\textsubscript{u} (this is the case with PDPA), then CI with molecular TT functions can only raise the energy of the polymeric 2A\textsubscript{g}. Since the polymer of Fig. 1 is for the sake of illustration only, this information can be used to further modify the basic design of the desired polymer (for example, replacing the double bonds of the sidegroups with triplet bonds would continue to give low E(1B\textsubscript{u}) but would increase E(2A\textsubscript{g})).

CI with higher energy TT diagrams of type (ii), can only increase E(2A\textsubscript{g}). To demonstrate this, first consider a new restricted basis in which we retain the HOMO/LUMO (HOMO–1/LUMO+1) MOs of odd (even) units. This system is equivalent to an ordered copolymer in which alternate monomers have larger one-electron gaps than in ethylene (e.g., polydiacetylene), and has higher relative E(2A\textsubscript{g}) than in t-PA. We can now visualize many similar systems, in which we retain various pairs of these four MOs on each unit. All such disordered copolymers also have higher E(2A\textsubscript{g}). CI with type (ii) TT diagrams effectively includes matrix elements between A\textsubscript{g}-type configurations within these new bases and the minimal basis A\textsubscript{g} configurations, and will therefore only increase E(2A\textsubscript{g}).

To summarize, transverse conjugation over a small number of bonds is one way to generate conjugated polymers with light emission in the IR. Excited state ordering conducive to light emission is a consequence of the reduction of the effective Hubbard repulsion due to delocalization over a molecular site. The system investigated here is the simplest example with this characteristic, but one can visualize many other such structures, including realistic materials like poly-isothianaphthene with a gap of 1.1 eV. We hope that our work will stimulate experimentalists to investigate derivatives of the latter or to synthesize new materials with the necessary structural features.

Work in Arizona was supported by NSF DMR-0101659, NSF ECS-0108696 and the ONR. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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