Electron-hole versus exciton delocalization in conjugated polymers:
the role of topology

S. Dallakyan,^a^ M. Chandross,^b^ and S. Mazumdar^a^
^a^Department of Physics, University of Arizona, Tucson, AZ, 85721, USA
^b^Sandia National Laboratories, Albuquerque, NM 87185, USA

Abstract

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 the requirement for such a material is that the exciton delocalization in the system be large, such that the optical gap is small. We develop a theory of exciton delocalization in conjugated polymers, and show that the extent of this can be predicted from the topology of the conjugated polymer in question. We determine the precise structural characteristics that would be necessary for light emission in the IR.

Key words: Polyacetylene and derivatives, Semi-empirical models and model calculations, Light sources.

A serious limitation in the field of polymer-based lasers arises from the fact that 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 \( 1B_u \) state in these. 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 excited state ordering \( E(2A_g) > E(1B_u) \), which is a consequence of enhanced effective bond alternation within the effective linear chain model for these systems [1]. Since enhanced bond alternation necessarily increases \( E(1B_u) \), it appears that strong PL is limited to systems with optical gaps larger than that of t-PA.

Our goal is to demonstrate that materials obtained by “site-substitution” of t-PA, in which the hydrogen atoms of t-PA are replaced with transverse conjugated groups will simultaneously have small optical gaps and \( E(2A_g) > E(1B_u) \). Initial work in this area by us was limited to the specific system poly-diphenylpolyacetylene (PDPA) [2,3], in which the hydrogen atoms of t-PA are replaced with phenyl groups. Because of chain-bending due to steric repulsion, PDPA have short conjugation lengths [4] and emit in the visible. Further, although we determined from our calculations that \( E(2A_g) > E(1B_u) \) in PDPA, because of the large number of atoms in the phenyl groups, our calculations were based on uncontrolled approximations. Here we have chosen a hypothetical system for which considerably improved many-body calculations can be done, and also, if the system can at all be synthesized, steric repulsion would be minimal and true long chain systems can be expected.

Our calculations below are for the substituted polyene shown in Fig. 1, with the hydrogen atoms of a 10-carbon atom polyene replaced with ethylene. We shall refer to this as the substituted polyene, and compare the excited state ordering in this system with the ordinary 10-carbon atom polyene. Our calculations are within the dimerized
Hubbard Hamiltonian

\[ H = -\sum_{j\sigma} t_j (c_j^\dagger \sigma c_{j+1} + h.c.) + U \sum_j n_{j\uparrow} n_{j\downarrow} \]  

where all terms have their usual meanings and \( t_j = 2.2 \text{ eV} \) and \( 2.6 \text{ eV} \) for single and double bonds, respectively. For both the polyene and the substituted polyene we increase the Hubbard \( U \) from zero (where \( E(2A_g) > E(1B_u) \)) and determine the critical \( U_c \) at which energy cross-over \( E(2A_g) < E(1B_u) \) occurs. For our speculation to be correct, (i) \( E(1B_u, \text{substituted}) \) must be smaller than \( E(1B_u, \text{unsubstituted}) \), and (ii) \( U_c(\text{substituted}) \) must be greater than \( U_c(\text{unsubstituted}) \). The latter would imply that for a fixed \( U \), \( E(2A_g, \text{substituted}) \) is higher than \( E(2A_g, \text{unsubstituted}) \).

Our calculations are based on the exciton basis valence bond method [5], within which the both the unsubstituted and substituted polyene are considered as coupled two-level systems, where the two levels are the HOMO and the LUMO of the unit cell (i.e. both calculations involve 10 MOs). This approach is exact for the polyene, but approximate for the substituted polyene. It is easy to prove that the \( U_c \), calculated within the approximate method is a lower limit for the true \( U_c(\text{substituted}) \). To prove this, we compare the exact Hückel energies of the 10-carbon substituted polyene with those calculated using the exciton basis. The exact (approximate) \( E(1B_u) = 1.02 \text{ (1.25) eV} \) and \( E(2A_g) = 1.59 \text{ (1.65) eV} \). Now, since \( E(1B_u) \) increases with \( U \), while \( E(2A_g) \) decreases (following an initial weak increase), it is seen from the above energies that the \( U \) at which the true \( E(1B_u) \) becomes larger than the true \( E(2A_g) \) must be higher than that calculated within the reduced basis set.

In Figs. 2(a) and (b) we have plotted \( E(1B_u) \) and \( E(2A_g) \) against \( U \) for the unsubstituted and the substituted polyene. We note that (i) \( E(1B_u, \text{substituted}) < E(1B_u, \text{unsubstituted}) \) for any \( U \), and (ii) \( U_c(\text{substituted}) \) is larger than \( U_c(\text{unsubstituted}) \) by \( \geq 1 \text{ eV} \). The reason why the \( 2A_g \) (1B_u) is higher (lower) in energy in the substituted system is as follows. In the strongly correlated electron model, the 1A_g has all sites singly occupied with electrons, and the 1B_u consists of a single doubly occupied site. This double-occupancy in the substituted polyene is delocalized over the entire transverse molecular unit, and thus the effective Hubbard correlation, \( U_{eff} \), is smaller. The lower \( U_{eff} \) reduces \( E(1B_u) \) and raises \( E(2A_g) \). Since the 1B_u is predominantly a singly excited configuration, while the correlated 2A_g consists of both single and double excitations, one then expects that there is no qualitative difference between the unsubstituted and substituted 1B_u wavefunctions at any \( U \), but a strong difference in the 2A_g wavefunctions. This is exactly what is seen from our calculations of the wavefunctions within the exciton basis.

Very similar results are obtained for \( N = 4, 6 \) and 8 carbons on the backbone polyene. Finite size scaling shows that considerably larger \( U_c \) in the substituted polyene is expected for \( N \to \infty \). We conclude that transverse site-substitution is one approach to obtain excited state orderings conducive to light emission in the IR. Whether or not the present system can be synthesized, we believe that the principle demonstrated here is general.

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