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Excitation Dynamics in Disubstituted Polyacetylene

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Recent advances in understanding the excited electronic states in π -conjugated polymers have led the research community to recognize the importance of the excited state ordering. The photoluminescence quantum efficiency, η , and the resonant third-order optical properties of these materials are determined by the relative energy and symmetry of a subset of the excited states, including a series of singlet excitations with odd (mB_u) and even (κA_g) parity lying below the continuum threshold. If the lowest A_g exciton ($2A_g$) is below the lowest $1B_u$ exciton, $E(2A_g) < E(1B_u)$, as in polymers with small effective dimerization, δ , then η is small because of the dipole forbidden character of the lowest singlet. Conversely, for $E(2A_g) > E(1B_u)$, as in polymers with large δ , η is large and these polymers might be considered as active materials for displays and laser-action applications.

We studied the excitation dynamics in films of disubstituted polyacetylene, a degenerate ground state conjugated polymer, using psec transient and steady state spectroscopies. The polymer is found to support charged and neutral topological soliton excitations concurrent with a strong, intrinsic photoluminescence band with quantum efficiency, η as high as ~50%; this leads to stimulated emission in thin films and lasing in cylindrical μ -cavities. These excitation properties are unique among polymers of both degenerate and non-degenerate ground state. The seeming contradiction of a degenerate ground state polymer with high η , is explained by the lowest excited state ordering.

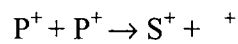
The degeneracy state of the disubstituted polyacetylene polymers was checked by electrochemical and chemical doping¹. Independent of the dopant concentration we observed upon doping a single doping induced absorption (DIA) band at about 1.1 eV, that was followed by pronounced infrared active vibrations, IRAV, at photon energy below 0.2 eV. The two DIA features grew together upon increasing the dopant

concentration. Since a single electronic DIA band shows that the injected charges are accommodated in the form of soliton excitations, that can exist only in polymers with degenerate ground state, then these doping induced results show that disubstituted polyacetylene polymers indeed have a degenerate ground state.

Next we studied the long-lived photoexcitations in thin films of several disubstituted polymers.

In pristine films we found a single photoinduced absorption (PA) band at 1.7 eV, or 2.1 eV depending on the polymer optical gap, where the lower energy PA band occurs in green polymers, whereas the highest PA occurs in blue polymers. We studied the spin state of these excitations by the technique of PA detected magnetic resonance (PADMR)². We found that the long-lived photoexcitations are correlated with spin $\frac{1}{2}$. Moreover since the PA band was not correlated with photoinduced IRAV we conclude that it is due to neutral photoexcitations. In this case we could identify the long-lived photoexcitations with spin $\frac{1}{2}$, neutral soliton.

The long-lived photoexcitations were found to be different upon photo-oxidation or doping with C₆₀ molecules. In these cases, due to photoinduced charge transfer into the high affinity traps, positive charges are left on the polymer chains. At low C₆₀ doping concentration we found³ two correlated PA bands at 0.2 and 2.4 eV, that are charged and therefore correlated with photoinduced IRAVs. We identified these PA bands as due to spin $\frac{1}{2}$ polarons, that traditionally show two intragap transitions. At high C₆₀ doping concentration, however we found that a third PA band dominated the photomodulation spectrum. This PA band occurred at 1.1 eV, similar to the DIA band due to charged solitons. We therefore identified this PA band as due to charged solitons that are created via the reaction



where P⁺ are positively charged polarons and S⁺, ₋⁺ are positively charged soliton-antisoliton pairs.

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- (2) M. Liess et al., SPIE **3145**, 179 (1997).
- (3) I. I. Gontia et al., Jour. Synth. Metals, **101**, 273 (1999).