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Excitation Dynamics in Disubstituted Polyacetylene

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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, $\eta \simeq 50\%$. This leads to stimulated emission in thin films and lasing in cylindrical μ cavities. The seeming contradiction of a degenerate ground-state polymer with high η is explained by the lowest excited-state ordering. [S0031-9007(99)09122-X]

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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 (PL) 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 excitons with odd (mB_u) and even (kA_g) parity lying below the continuum threshold [1]. 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 [2]. 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.

Among the polymers with extremely weak PL are trans-polyacetylene [t-(CH)$_x$] [3], its monosubstituted derivatives [4], polyheptadiyne [5], and polygranniline [6], which are considered nonluminescent conjugated polymers (non-LCP). These polymers have a degenerate ground-state (DGS) structure [Figs. 1(a) and 1(b)] and as such support soliton (S) excitations, both neutral [S^0, Fig. 1(c)] and charged [$S^{\pm}$, Fig. 1(d)]. Based on this correlation, it is usually assumed that DGS polymers cannot exhibit PL. This was traditionally explained by the soliton model, in which the primary excitations are soliton-antisoliton ($S\bar{S}$) pairs [7,8]. However, when electron correlations are taken into account [9,10], the weak PL in these DGS polymers can be alternatively explained by simply assuming $E(2A_g) < E(1B_u)$. This is certainly true for t-(CH)$_x$, where $E(2A_g) = 0.96$ eV and $E(1B_u) = 1.5$ eV [11]. In addition, it is also known that energy relaxation is larger in non-LCP compared to that in LCP [12]. This gives rise to a larger PL Stokes shift in DGS polymers. For example, in t-(CH)$_x$ it was determined [11,13] that the weak IR PL peak [emitted from the relaxed $1B_u$ state, denoted hereafter as $(1B_u)_r$] is at 1.24 eV, compared to $E(1B_u) = 1.5$ eV; this amounts to a 0.26 eV Stokes shift. Thus, it may be possible to find DGS polymers with strong PL, provided that either $E(1B_u) < E(2A_g)$ or $E(1B_u)_r < E(2A_g)$. However, so far none have been found.

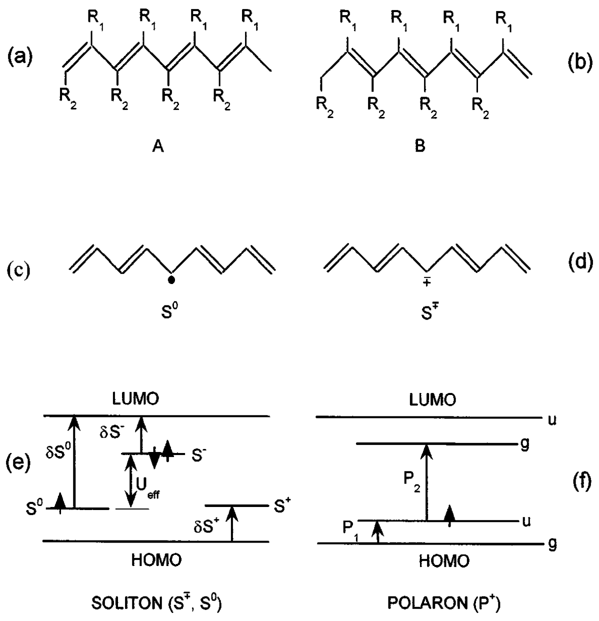

FIG. 1. (a),(b) The two degenerate ground-state structures (A and B) of PDPA, where R_1 and R_2 are phenyl derivative side groups. (c),(d) Neutral S^0 and charged $S^{\pm}$ soliton excitations, respectively. (e),(f) The energy levels and optical transitions of S^0, $S^{\pm}$, and polaron excitations, respectively; U_{eff} is the effective electron correlation energy and HOMO (LUMO) is the highest occupied (lowest unoccupied) molecular orbital.

In this Letter we discover a new, strongly luminescent DGS polymer, a representative of the novel *family* of disubstituted polyacetylenes $(CR_1CR_2)_x$ (Fig. 1), where R_1 and R_2 are phenyl derivatives (CH_3, C_2H_5, and C_6H_{13}), denoted hereafter as PDPA [14]. In particular, we have investigated the excitation dynamics of a PDPA derivative, where R_1 is a phenyl group and R_2 is a phenyl group attached to butyl [Fig. 2(b), inset] referred to as PDPA-*n*Bu. In our studies we have employed steady-state and ps transient spectroscopies, such as photoinduced absorption (PA), PL, and doping-induced absorption (DA). We show that PDPA-*n*Bu supports both charged and neutral soliton excitations, making it a member of the DGS polymer class. On the other hand, we discovered that it also shows a strong, intrinsic PL band with $\eta \simeq 50\%$, which may be used to produce microlasers (μ lasers) in the green spectral range.

Doping was performed either by exposing the film to iodine vapor forming $(\text{polymer})^+I_3^-$ or, electrochemically, by forming $(\text{polymer})^+BF_4^-$. PA and PL were excited by either an Ar^+ laser at 458 nm or a monochromatized xenon lamp, and probed in the spectral range from 0.1 to 3.4 eV. In order to determine the spin state of the various photoexcitations, we used the PA detected magnetic resonance (PADMR) technique [15], with μ waves at $\simeq$3 GHz. Magnetic field-swept H-PADMR spectra (at fixed wavelength λ) are presented, as well as λ-PADMR spectra (at fixed H while sweeping λ).

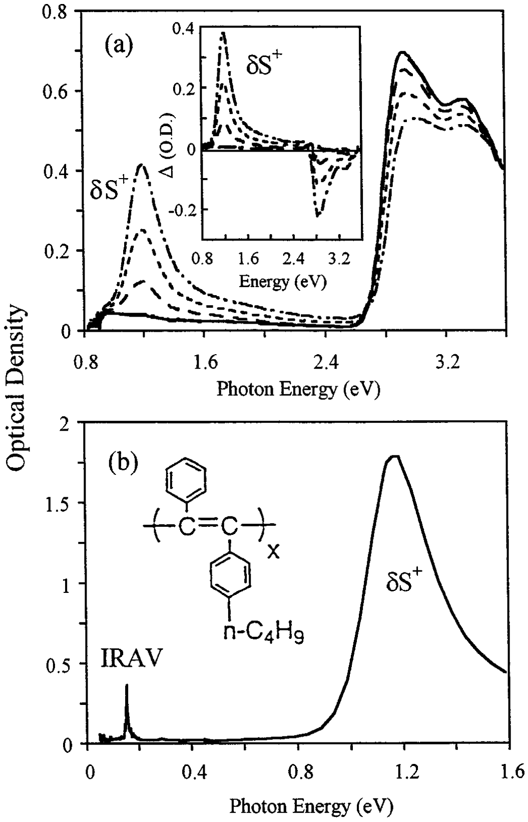

FIG. 2. Evolution of DA spectra of PDPA-*n*Bu upon electrochemically doping with BF_4^- (a) and by vapor doping with I_3^- (b). The inset of (a) shows the difference in DA spectra and the inset to (b) shows the PDPA-*n*Bu repeat units. δS^+ and the IRAV transitions are assigned.

The transient PL and lasing measurements were obtained using a mode-locked Nd:YAG regenerative laser amplifier, tripled at 3.45 eV, with 120 ps pulse duration and up to 100 μJ energy per pulse. For the PL decay we used a streak camera with 10 ps time resolution. Neat thin films of PDPA-*n*Bu were spun cast on quartz or single crystal potassium bromide substrates from polymer solutions in chloroform. The polymer μ-ring lasers were obtained by dipping commercially available optical fibers into *saturated* chloroform solutions, forming thin polymer rings around the glass cylindrical core. The emitted light was collected in the plane of the μ-ring with a spectral resolution of $\simeq$1 Å.

One way to identify DGS polymers is by studying their elementary excitations. Degenerate ground-state polymers support topological soliton excitations ($S^0, S^\pm$) which are in the form of a domain wall separating the two DGS structures [16]. These quasiparticles may be identified by their reversed spin-charge relationship and optical transitions [3]. S^0 carries spin-$\frac{1}{2}$, whereas $S^\pm$ are spinless. Also, both S^0 and $S^\pm$ show a single absorption band, δS, below the optical gap. The energy difference $\delta S^0 - \delta S^\pm$ is the soliton effective correlation energy U_{eff} [Fig. 1(e)] [17]. Excitations in non-DGS polymers, on the contrary, may be accommodated as charged polarons ($P^\pm$) [3], which carry spin-$\frac{1}{2}$ and have *two* absorption bands below the gap [Fig. 1(f)] [18].

We show that PDPA-*n*Bu supports soliton excitations and therefore has DGS structure. Figure 2 shows the evolution of the absorption spectrum $\alpha(\omega)$ upon BF_4^- (a) and I_3^- (b) doping. Upon BF_4 doping, only a *single* doping-induced absorption band at $\simeq$1.2 eV appears and the interband absorption bleaches. From the difference in DA spectra in Fig. 2(a) (inset), it is seen that the total oscillator strength is conserved upon doping [3], so that an additional DA band below 0.8 eV is improbable. This is verified upon I_3^- doping, using a Fourier-transform infrared spectrometer down to 500 cm^{-1}. As can be seen in Fig. 2(b) there is only a single DA band at $\simeq$1.2 eV, accompanied by an infrared active vibration (IRAV) band at $\simeq$0.15 eV, which is a clear signature for doping-induced charged excitations [19]. Using an *in situ* ESR spectrometer, we found that only seven spins (at $g \simeq 2$) per 1000 electron charges were created upon doping, showing that the doping-induced charged species are practically spinless. Then, based on the reversed spin-charge relationship and the single DA band found below the gap, even at low doping levels, we conjecture that S^+ excitations are formed in PDPA-*n*Bu upon p-doping.

Soliton excitations can also be created in PDPA-*n*Bu upon photoexcitation, as shown in Fig. 3. Pristine

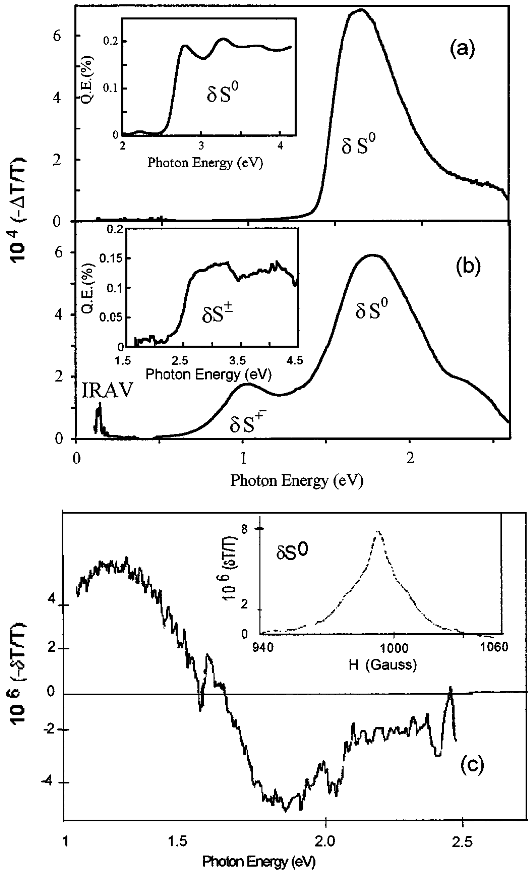

FIG. 3. Photoexcitations in PDPA-*n*Bu. (a),(b) The PA spectra of pristine and photo-oxidized films, respectively, where the transitions $\delta S^\pm$ and δS^0 are assigned. Insets of (a) and (b) show, respectively, the excitation dependence spectra of δS^0 and $\delta S^\pm$. (c) λ-PADMR spectrum at $H = 990$ G. Inset: H-PADMR spectrum probed at 1.7 eV.

PDPA-*n*Bu films show a single long-lived PA band at $\simeq$1.7 eV [Fig. 3(a)] with no correlated photoinduced IRAV, indicating neutral photoexcitations. Comparing it with the DA band shown above, we estimate a low quantum efficiency (QE) of $\simeq$0.2%. Furthermore, PADMR studies of this sample reveal that this long-lived PA band is associated with spin-$\frac{1}{2}$ excitations. The H-PADMR spectrum [Fig. 3(c), inset] measured at 1.7 eV shows a correlated spin doublet at $H_0 = 990$ G ($g \simeq 2$); the λ-PADMR [Fig. 3(c)], measured at H_0, tracks this PA band. Similar to t-(CH)$_x$ [18], there is also a negative PADMR tracking δS^+ in this film. Therefore, the long-lived PA in pristine PDPA-*n*Bu films is due to neutral species with spin-$\frac{1}{2}$, and may be identified as the δS^0 transition [Fig. 1(e)]. The δS^0 QE per absorbed photon [Fig. 3(a), inset] basically shows a step-function response with very low QE at the optical band edge, indicating that S^0 photogeneration in pristine films is small and correlated with thermalized excitons.

However, when the pristine film was exposed to either moderate laser light or sun light for a few hours at ambient atmosphere, photo-oxidation-related impurities caused dramatic changes in the PA spectrum [Fig. 3(b)]. In addition to the δS^0 PA band, the spectrum also contains a PA band at $\simeq$1.1 eV together with a correlated IRAV at $\simeq$0.13 eV. The similarity with the DA spectra in Fig. 2 leads us to identify the PA band at 1.1 eV with $\delta S^\pm$ and conclude that $S^\pm$ are also photogenerated in photo-oxidized films, with QE $\simeq$ 0.1%. The excitation dependence of $\delta S^\pm$ QE is shown in the inset of Fig. 3(b). Similar to δS^0 QE spectrum in Fig. 3(a), the $\delta S^\pm$ QE spectrum here also abruptly increases at the optical band edge, indicating that $S^\pm$ photogeneration in photo-oxidized films is a competing process to S^0 photogeneration, and is also correlated with thermalized excitons. Moreover, using the relation $U_{\text{eff}} = \delta S^0 - \delta S^\pm$ [17] [Fig. 1(e)] and $\delta S^0 = 1.7$ eV and $\delta S^\pm = 1.1$ eV, we find $U_{\text{eff}} = 0.6$ eV.

PDPA-*n*Bu films also show a strong PL band in the green/yellow spectral range, with full width at half maximum (FWHM) of $\simeq$100 nm [$\simeq$0.4 eV, see Fig. 4(a)] that has already been used for the fabrication of light-emitting diodes with remarkable electron/photon efficiency [20].

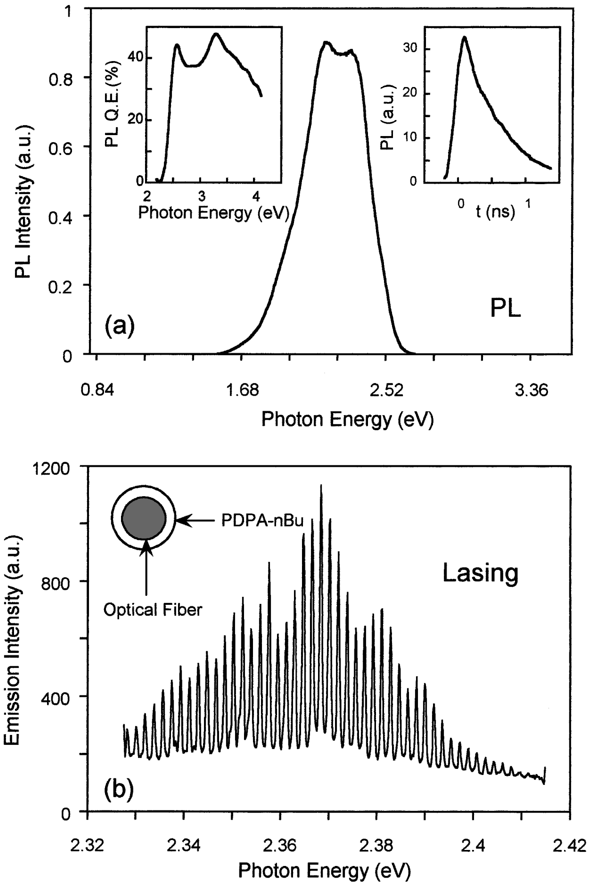

FIG. 4. (a) PL spectrum in PDPA-*n*Bu film; the insets show the excitation dependence of the PL QE and the PL transient decay, respectively. (b) Laser modes in a PDPA-*n*Bu μ-ring (shown in the inset) wrapped around a 128 μm diameter optical fiber core. The spectral resolution is $\simeq$1 Å.

The 0-0 PL transition [or $(1B_u)_r$] is at 2.5 eV, indicating a moderately large Stokes shift ($\simeq$0.25 eV), comparable to that found in t-(CH)$_x$ [13]. The absolute PL QE, excited at $\hbar\omega = 2.7$ eV and measured with an integrating sphere, was found to be $\eta \simeq 50\%$. The η excitation spectrum [Fig. 4(a), inset] is similar to the δS^0 QE spectrum [Fig. 3(a)] and shows a step-function increase at 2.5 eV which, however, has high QE, indicating that the PL is an intrinsic process.

We also measured the PL decay at low excitation intensity [Fig. 4(a), inset], and found an exponential decay with lifetime $\tau \simeq 600$ ps. In order to find the radiative lifetime τ_r, we use the following relation [21]: $\eta = b\tau/\tau_r$, where b is the $(1B_u)_r$ photogeneration quantum yield. Assuming $b \simeq 1$ [21], and using the experimental values $\eta = 50\%$ and $\tau \simeq 0.6$ ns, we find $\tau_r \simeq 1.2$ ns. This is close to τ_r of poly(p-phenylene vinylene) (PPV) based polymers [21], showing that the $1B_u$ exciton transition dipole moment and wave function extent in PDPA-nBu are similar to those in PPV. This is also in agreement with the intrinsic character of the PL mechanism in PDPA-nBu.

Neat PDPA-nBu films show amplified spontaneous emission at high excitation intensity I above a threshold intensity, $I_{\mathrm{th}} \simeq 1\ \mu\mathrm{J/mm}^2$ [22], similar to I_{th} found in PPV films. Under these conditions, the PL band shows a dramatic spectral narrowing from FWHM of 100 nm (0.4 eV) at low I to less than 10 nm (40 meV) at $I > I_{\mathrm{th}}$. The process can be used to produce μ-lasers, provided a feedback mechanism exists. This is shown in Fig. 4(b), where we show the emission spectrum of a PDPA-nBu μ-ring laser deposited around an optical fiber with a core diameter of 128 μm [Fig. 4(b), inset]; I_{th} in this case was extremely small, of order 10 nJ/pulse [23], again in agreement with PPV μ-lasers. The laser resonant modes are resolution limited (<1 Å), showing a relatively high quality factor Q of order 5000.

In order to explain the seeming contradiction in the photoexcitation properties of PDPA-nBu that are mainly excitons with high η, but also form neutral and charged solitons, with low QE, we note that there are two possible relaxation channels in DGS polymers following excitations into the $1B_u$ [10]. These are the ionic channel, in which $1B_u$ relaxes to $(1B_u)_r$, and the covalent channel, in which $1B_u$ relaxes to $2A_g$ by emitting an odd parity phonon [10]. Excitations in the ionic channel may luminesce, whereas excitations in the covalent channel may decompose into a pair of triplets [24], which further decompose into a quartet of S^0 excitations [25]. The QE of these two channels depends on the order of the lowest lying excitonic states. If $E(2A_g) < E(1B_u)$, the covalent channel dominates. This may be the case in t-(CH)$_x$ [11], where S^0 are photogenerated with high QE [15] and PL is extremely weak [13]. On the other hand, if $E(2A_g) > E(1B_u)$ or $E(2A_g) > E(1B_u)_r$, the ionic channel dominates and the polymer may show PL with high QE, as is the case here. However, whether $E(2A_g) > E(1B_u)$ or $E(2A_g) > E(1B_u)_r$ in PDPA-nBu remains to be determined in future work.

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