The role of triplet states in the emission mechanism of polymer light-emitting diodes

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The blue emission of polyfluorene (PF) based light-emitting diodes (LEDs) is known to degrade due to a low energy green emission, which hitherto has been attributed to oxidative defects. By studying the electroluminescence from ethyl-hexyl substituted PF LEDs in the presence of oxygen and in an inert atmosphere, and by using trace quantities of paramagnetic impurities (PM) in the polymer, we show that the triplet states play a major role in the low energy emission mechanism. Our time-dependent many-body studies show that there is a large cross-section for the triplet formation in the electron-hole recombination process in presence of PM, and intersystem crossing from excited singlet to triplet states.

Defects in organic semiconductors impede charge transport and emission mechanisms in organic light-emitting diodes (LEDs). Emission energies lower than the π-π^* gap in conjugated polymers (CP) have been attributed to chemical and structural defects, aggregates and interchain interactions. Polyfluorenes (PF) have emerged as an especially attractive CP due to their strong blue emission, high charge carrier mobility, and thus great prospects for device application [1]. Molecular attributes such as local structure and side chain conformations in these systems strongly impact transport and device characteristics. In the PF family, poly (9,9-(di *n, n*-octyl) fluorene) (PF8) and poly (9,9-(di ethyl hexyl) fluorene) (PF2/6) have received a lot of attention mainly due to their mesomorphism and crystalline phases [2, 3, 4, 5].

A controversial subject in PFs has been the physical mechanism behind a broad green band in the photoluminescence (PL) and electroluminescence (EL). There seems to be a general consensus that its origin lies in keto defect (9-fluorenone) sites. Such defects can be accidentally incorporated into the π-conjugated PF backbone due to the presence of nonalkylated or monosubstituted fluorene sites during synthesis or as a result of a photo-oxidative degradation process [6]. However, the exact mechanism of the green emission is heavily debated; it has been attributed to a direct emission from flourenone defects [7], an intramolecular charge transfer complex [8], and due to inter-chain excited species [9].

The inset of Fig. 1(b) shows a monomer unit of PF2/6; the bridging carbon atom is the site of a keto defect where an oxygen atom replaces the ethyl-hexyl group. The nature of the PL and EL spectra in PFs due to these defects may also differ. Differences in PL and EL are often observed in smaller molecules [10]. A recent work shows that charge-dipole interactions stabilize energy states which are lower than the singlet excited states, accounting for a red-shifted EL emission [11].

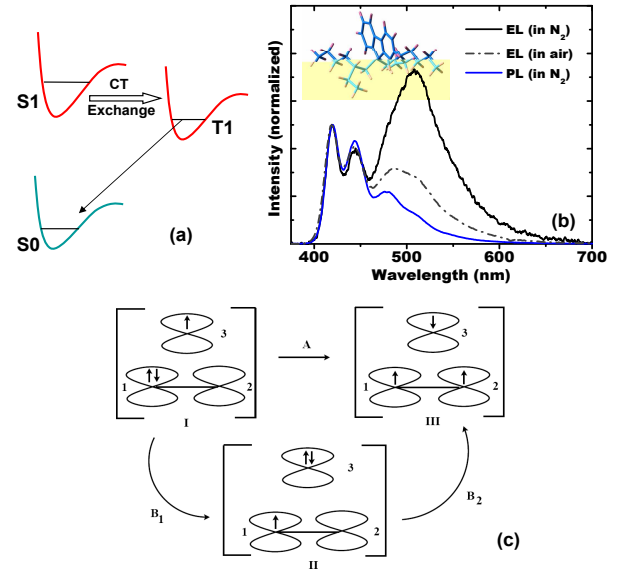In this Letter we show that charge transfer (CT) and exchange pathways cause mixing of the excited singlet

FIG. 1: (a) Schematic of the conversion of singlet to triplet states. (b) EL and PL spectra from a PF2/6 LED. The solid lines are the EL and PL spectra from a device fabricated in N_2 atmosphere and the dotted line represents the EL spectrum from an LED fabricated under ambient conditions. Inset shows the structure of a fluorene monomer with ethyl-hexyl side group. (c) The charge transfer (B_1 and B_2) and the exchange (A) pathway for conversion of the singlet excited state of an ethylene molecule (1-2) to the triplet state by a paramagnetic impurity (3) are depicted here. The charge transfer pathway is mediated by the transfer integrals (t_{31} for B_1 and t_{23} for B_2) and the exchange pathway is mediated through the two-electron integral [13|23] in Eq.2.

(S_1) and the triplet (T_1) states, as shown schematically in Fig. 1(a). It opens up possible decay channels from T_1 to the singlet ground state (S_0), which is otherwise a forbidden transition. This phenomenon is more generic than previously thought and may account for the low energy emission mechanism in a host of short and long-chain CP and molecules. The intensity of the low-energy EL spectrum (490 nm-560 nm) in PF2/6 LEDs differ

dramatically for samples prepared in air (O_2), N_2, and doped with paramagnetic impurities (PMs). A comparison of our experimental results with theory clearly shows that the low energy EL emission can be attributed to $T_1 \rightarrow S_0$ type transitions, and not necessarily to keto defects as suggested in previous works.

The LEDs were fabricated by first spincoating 80 nm of poly(ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) onto patterned indium tin oxide (ITO) glass slides, on top of which 100 nm of PF2/6 was spincoated from a toluene solution (10 mg/ml), and capped by Ca/Al. Each sample supported 15 devices with area 4 mm^2, and was encapsulated prior to measuring EL and PL. The devices under N_2 atmosphere were fabricated inside a N_2 glovebox including the cathode evaporation and encapsulation. The ambient condition LEDs were obtained by first spincoating PF2/6 in an ambient atmosphere, followed by the rest of the steps in a N_2 glovebox. Furthermore, metal doped LEDs were fabricated by introducing trace quantities of Cu (II) (copper perchlorate) and a Pd complex in the PF2/6 solution, both in ambient and N_2 atmosphere. Introduction of PMs in PF2/6 results in an electron-hole recombination (e-hR) or intersystem crossing (ISC) to the triplet states, mediated by both exchange and CT mechanisms.

Our theoretical model system consists of a finite polyene chain and a PM. The e-hR process leading to excited singlet S_n or triplet state T_m of a polyene is modeled with and without a paramagnetic atom. The initial positively and negatively charged polyenic states are the eigenstates within the Pariser-Parr-Pople (PPP) model [12] with standard parameters and Ohno potentials [13] for long range Coulomb interactions. The metal atom is described by a single orbital or two degenerate orbitals, with one unpaired electron in both cases. The PPP Hamiltonian for the molecule is given by [14]:

$$H_{polymer}^{PPP} = \sum_i \alpha_i \hat{E}_{ii} + \sum_{\langle ij \rangle} t_{ij} \hat{E}_{ij} + \frac{1}{2} \sum_i U_i \hat{n}_i (\hat{n}_i - 1)$$
$$+ \sum_{i>j} V_{ij} (\hat{n}_i - z_i)(\hat{n}_j - z_j), \quad (1)$$

where $\hat{E}_{ij} = \sum_{ij} \hat{a}_{i,\sigma}^\dagger \hat{a}_{j,\sigma}$; $\hat{a}_{i,\sigma}^\dagger$, $\hat{a}_{j,\sigma}$, and $\hat{n}_i$ are the usual fermionic creation, annihilation, and number operators, respectively. α_i and t_{ij} are respectively the site energies and hopping integrals, $\langle ij \rangle$ denotes the bonded pair, U_i denotes on-site correlations, and V_{ij} the intersite interactions. The Hamiltonian of the magnetic impurity is $H_P = \sum_\sigma \alpha_1 \hat{a}_{1,\sigma}^\dagger \hat{a}_{1,\sigma} + (U_P/2)\hat{n}_P(\hat{n}_P - 1)$. The total spin of the full system (impurity and the polyene radical ions, M^+ and M^-) are conserved, although the individual moieties can undergo a change in spin state. The e-hR in the absence of PM occurs due to the CT type interactions between the chains. In the presence of PM the recombination occurs due to both one electron (CT pathways) and two-electron (exchange pathways) interactions

[15, 16] between the impurity and the polymer chain, schematically shown in Fig. 1(c). Both these pathways are incorporated through the interaction Hamiltonian,

$$H_{int} = \sum_{ij} t'_{ij} \hat{E}_{ij} + \frac{1}{2} \sum_{ijkl} [ij|kl] \left(\hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} \right), \quad (2)$$

where t'_{ij} is the one-electron transfer integral giving rise to the CT process and $[ij|kl]$ is the two electron integral in charge cloud notation.

Wave-packet propagation technique is employed to study the electronic process involving the polyene ion-radicals and the magnetic impurity. The initial state of the e-hR process is modeled as a direct product of the ground states of a positive (M^+) and a negative (M^-) polyene radical ion along with a PM, and is given by

$$\Psi_{e-hR}(0) = \frac{1}{\sqrt{6}} |\frac{1}{2}, -\frac{1}{2}\rangle_{M^+} \otimes |\frac{1}{2}, \frac{1}{2}\rangle_{M^-} \otimes |\frac{1}{2}, \frac{1}{2}\rangle_{PM}$$
$$+ \frac{1}{\sqrt{6}} |\frac{1}{2}, \frac{1}{2}\rangle_{M^+} \otimes |\frac{1}{2}, -\frac{1}{2}\rangle_{M^-} \otimes |\frac{1}{2}, \frac{1}{2}\rangle_{PM}$$
$$- \frac{2}{\sqrt{6}} |\frac{1}{2}, \frac{1}{2}\rangle_{M^+} \otimes |\frac{1}{2}, \frac{1}{2}\rangle_{M^-} \otimes |\frac{1}{2}, -\frac{1}{2}\rangle_{PM} \quad (3)$$

All states are labeled by the spin quantum numbers S and M_s. $|1/2, -1/2\rangle_{M\pm}$ is the ground state of the positive (negative) ion-radical expressed as linear combination of the valence bond (VB) functions which span the doublet space of the ion-radical Hamiltonian. The wave-packet, $\Psi_{e-hR}(0)$, is time evolved in discrete time steps by the time-dependent Schrödinger equation using the multistep differencing scheme (MSD) [17], with the total Hamiltonian given by $H_{M^+}^{PPP} + H_{M^-}^{PPP} H_P + H_{int}$. The evolved state, $\Psi_{e-hR}(t)$, is then projected on to the direct product of excited singlet (for singlet pathway) or triplet (for triplet pathway) states, the singlet ground state of the neutral molecule and the PM.

The probability for polaron recombination, P_{T_m/S_m}, through triplet/singlet pathways is given by $|\langle \Psi_{e-hR}(0) | \Psi_{e-hR}^{S/T}(t) \rangle|^2$. Phosphorescence intensity is a measure of the cross-section for radiative decay of the lowest triplet to the ground state. The lowest triplet state is obtained from any of the higher lying triplet states via internal conversion in the triplet manifold according to Kasha's rule [18]. The time integrated yield of the triplet/singlet channel, $I_{T/S} \equiv \sum_m \int_0^{T_{max}} P_{T_m/S_m}(t) dt$, is thus a measure of the phosphorescence/fluorescence intensity in EL measurements.

All EL and PL spectra have been normalized to the 0-0 vibronic peak. Figure 1(b) compares the EL spectra of two PF2/6 LEDs, one prepared under ambient condition and the other prepared in N_2 atmosphere. The intensity of green emission at 514 nm is substantially higher for the device prepared in N_2 atmosphere; the green EL emission is quenched for devices prepared in O_2 atmosphere. Two batches of PF2/6 were used in this study.

Figure 2 represents the EL and PL spectra from PF2/6 devices (with PMs) utilizing the slightly higher mol. wt. sample compared to Fig. 1.

Figure 2 (a) and (b) show the EL and PL spectra from Pd complex incorporated PF2/6 devices fabricated under N_2 and ambient atmosphere, respectively. Fig. 2 (c) shows all EL spectra including the devices where trace concentration of Cu(II) was introduced. Although the green EL emission from the high mol. wt. sample is lower than the low mol. wt. sample (Fig. 1 (b)) in N_2 atmosphere, the devices prepared with the high mol. wt. sample under O_2 atmosphere have reduced green emission. The intensity of the green emission is very much lower in the PL spectrum compared to the EL spectrum in both cases. If the emission was due to oxidative defects, one would expect the devices prepared in air to show a higher EL intensity. Besides, the PL and EL spectra would not be so drastically different as observed.

The EL and PL spectra shown in Figs. 1 and 2 are representative of at least 50 devices. We note that the PL spectra are obtained from the actual devices and since the devices were encapsulated, there is no additional occurrence of photo-oxidation during the measurement. Incorporation of PMs quench the PL emission in both N_2 and ambient environments (solid green lines in Fig. 2 (a) and (b)). A paramagnetic metal significantly enhances the triplet exciton yield; hence it is not surprising that the green emission is enhanced for Pd complex incorporated LEDs fabricated under N_2 and ambient conditions compared to as-is PF2/6 LEDs. The 514 nm emission is significantly higher for the N_2 fabricated device compared to the device fabricated under ambient atmosphere. This is expected since the presence of oxygen is known to quench the triplet excitons [19].

The green emission is very broad (490-560 nm) spanning the region of the 0-2 vibronic peak. The EL emission of the ambient PF2/6 device has a clearly resolved 0-2 vibronic peak at 480 nm, shown by the dotted line with a shoulder at 514 nm; the latter is further enhanced in the device fabricated in N_2 atmosphere (Fig. 2 (c)). The EL spectra of the two Cu(II)-incorporated PF2/6 LEDs are shown in Fig. 2 (c). The 514 nm emission is slightly reduced for the device fabricated in O_2.

Our experimental results are corroborated by the theory very well. The singlet and triplet state yields for butadiene calculated in presence and absence of PM are presented in Table I. The singlet to triplet state conversion by ISC pathway in presence of paramagnetic metal is also performed for polyenes of different sizes; only the octatetraene results are presented here. The polyene chains are modeled using standard PPP parameters for Carbon [14]. The butadiene units are placed end-on, 3.0Å apart and the paramagnetic site is located at 4.0Å on the perpendicular bisector of the full polyene system. The PM is modeled using either one or two d-orbitals with the Hubbard potential, U = 8.0 eV, α varying between -5.0

TABLE I: Singlet and triplet yields ($I_{T/S}$) in e-hR (for a pair of butadienes) and ISC (for octatetraene) in presence[1] and absence[2] of PM. Triplet yields in ISC are from the first excited state ($2A_g$).

Pathways	Site energy of PM(eV)	I_T Nondeg.	I_T Deg.	I_S Nondeg.	I_S Deg.
ISC	5.0	0.29	0.23		
e-hR[1]	5.0	12.43	0.89	4.91	0.83
e-hR[2]	-	0.44		1.82	

eV to 5.0 eV, bond-bond repulsion integrals $[ij|kl] \sim 0.5$ eV for the nearest neighbor pair $\langle ij \rangle$, $\langle kl \rangle$, and $t' \sim 0.2$ eV. These parameters are consistent with photo-emission spectroscopy data [20] for 3d/4d orbitals of metals which are 3 to 5 eV above the carbon 2p orbitals. The triplet yields are only weakly dependent upon the site energies. The higher yield of triplets has been observed when unpaired electron on the paramagnetic moiety is in a pair of degenerate orbitals. In the absence of PM the e-hR process yields more singlets than triplets. The triplet yield in presence of PM is much higher in e-hR process compared to the ISC pathway. Furthermore, the singlets formed in EL can be converted into triplets by ISC mechanism in the presence of PMs, which subsequently undergo internal conversion to the low energy T_1 from which phosphorescence may occur.

Our experimental results are consistent with the above; the intensity of the 514 nm EL peak is higher when doped with Pd complexes compared to Cu(II) salts (Fig. 2 c). In PL, the ISC is the only mechanism for the production of triplets. For this the singlet exciton must be in the vicinity of the PM, which at low impurity concentration is less probable. Hence we do not observe enhancement in PL green emission intensity. We have also calculated the quenching probability of triplet states in the presence of a paramagnetic oxygen molecule. Our calculations show that there is substantial quenching of the triplet excitons by O_2 which we attribute to the observed low intensity of green emission in samples prepared under ambient conditions with or without metal centers.

Geminate recombination of polaronic pairs result in the formation of both singlets and triplets, in systems with or without defects. Our calculations show that oxygen molecules annihilate the triplets while PMs generate triplets with high probability either from singlet excited states via ISC or from e-hR process. The broad green emission may be attributed to vibronic broadening and the triplet states of keto defects. ZINDO (Zerner's Intermediate Neglect of Differential Overlap) calculations carried out for a fluorene dimer with one or no keto defect show that the system with keto defect has a triplet state at 2.37 eV (close to our experimental results) while that without a keto defect has a triplet state at 2.89 eV. Thus
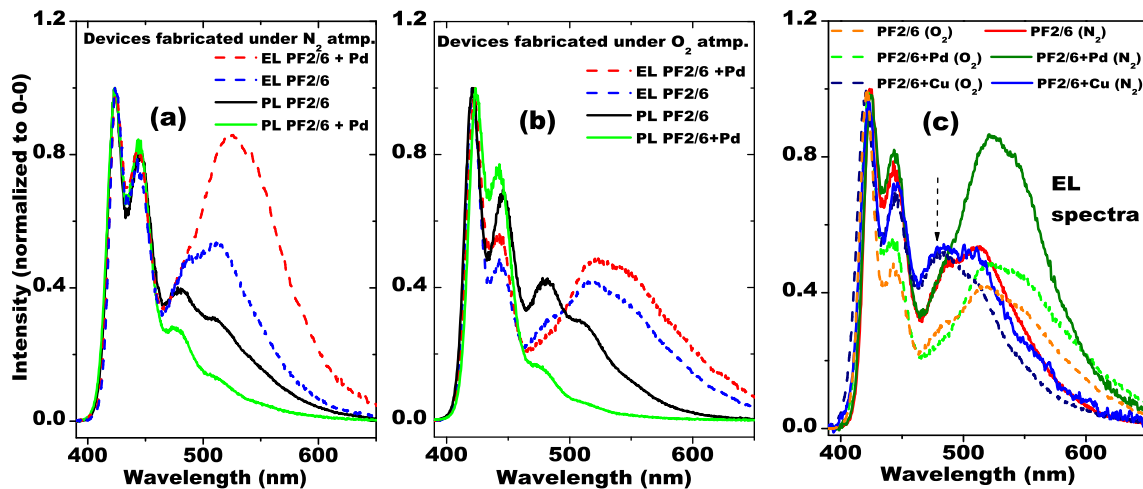
FIG. 2: EL and PL spectra of PF2/6 LEDs (a) fabricated in N_2 atmosphere, with and without Pd and (b) fabricated under ambient conditions, with and without Pd. (c) EL spectra of all PF2/6 LEDs fabricated in ambient and N_2 atmosphere; the dashed spectra represent devices that were fabricated under ambient conditions.

the green emission could occur from the triplet state created in the vicinity of a keto defect due to migration of the free triplet to a keto defect site. Electrophosphorescence has indeed been observed at low temperatures in PFs using time-resolved detection techniques [21]; our work clearly shows a large cross-section of triplets in the eh-R process, particularly in the presence of PM.

In summary, our studies show that the low energy EL emission in the PF system is from triplet excitons. This is corroborated by experimental studies on LEDs prepared in N_2 atmosphere and ambient conditions with different transition metal and ion dopants, and theoretical studies of ISC and electron hole recombination in the presence of PMs as well as triplet state quenching by O_2. The dopants provide both exchange and charge transfer pathways to convert singlet to triplet excitons in PF systems with and without keto defects. Such processes are not just restricted to PF systems but may explain the low energy EL emission in a number of conjugated polymers.

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