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

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Abstract – 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 (EL) 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 a large cross-section for the triplet formation in the EL process in the presence of PM, primarily due to electron-hole recombination processes.

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Introduction. – Defects in organic semiconductors impede charge transport and emission mechanisms in organic light-emitting diodes (LEDs). Emission energies lower than the $\pi-\pi^*$ 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 [2-5].

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 $\pi$-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 fluorenone 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. In case of PFs, the low-energy luminescence is routinely attributed to the presence of keto defects. Our experimental results cast doubt on this as the source of low-energy EL. Although in most cases both the PL and EL spectra are expected to be similar, exceptions are quite common in literature and crucially depend upon the relative energy of the charge transfer state compared to the lowest singlet excited state. Thus, similar EL and PL spectra are observed if the energy of charge transfer state is much higher compared to that of lowest singlet excited state, whereas on the contrary, a marked difference between the two luminescence is expected if the energy of charge transfer state formed during the electroluminescence is below the lowest singlet state [10]. In this case, the origin of the low-frequency EL emission may be attributed to various solid-state interactions like charge-dipole interactions and electronic polarizibility which predominantly stabilizes the charge transfer state [11].

In this letter we show that charge transfer (CT) and exchange pathways cause various dynamic processes like intersystem crossing (ISC) and electron-hole recombination
from a LED prepared in air. Inset shows the structure of a integrals (pathway for conversion of the singlet excited state of an defects as suggested in previous works. measured with the Ocean Optics 2000 spectrometer. LEDs Ocean Optics 2000 spectrometer. The EL spectra were also measured with a HeCd laser and were measured by an PL spectra were excited with the 325 nm line of a HeCd laser and were measured by an PL spectra were excited with the 325 nm line of a HeCd laser and were measured by an PMs. Enhancement of the low-energy EL peak in the presence of PMs reflects the triplet nature of the peak. This is further confirmed by quenching of the EL peak in O2 atmosphere. Similar to triplet annihilation by paramagnetic O2, the PM also results in slight quenching of the EL emission. Thus a comparison of our experimental results with theory clearly shows that the low-energy EL emission can be attributed to (T1 → S0)-type transitions, and not necessarily to keto defects as suggested in previous works.

**Experiment.** The PL spectra were excited with the 325 nm line of a HeCd laser and were measured by an Ocean Optics 2000 spectrometer. The EL spectra were also measured with the Ocean Optics 2000 spectrometer. LEDs were fabricated by first spincoating 80 nm of PEDOT-PSS onto patterned indium tin oxide 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 (see ref. [12] for details on fabrication and device structure). Each sample supported 15 devices with area 4 mm2, and was encapsulated prior to measuring EL and PL. The devices used under N2 atmosphere were fabricated inside a N2 glovebox including 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 N2 glovebox. We point out that the only difference in the devices fabricated in inert atmosphere versus devices fabricated in air was the spincoating stage of the polymer. The electrode deposition and encapsulation were all done in the N2 glovebox. Since all devices were encapsulated, none of the devices were exposed to water or oxygen during electrical measurement. Metal-doped LEDs were fabricated by introducing trace quantities of Cu (II) (copper perchlorate) and a Pd complex (triphenylphosphine Pd) in the PF2/6 solution, both in ambient and N2 atmosphere. Introduction of PMs result in an e-hR or ISC to the triplet states, mediated by both exchange and CT mechanisms.

**Theory.** Here we propose a theoretical model to describe various dynamical processes such as ISC and e-hR consisting of a finite polyene chain and a PM. We describe the e-hR process leading to excited singlet S1, or triplet state Tm of a polyene both in the presence and in the absence of a paramagnetic atom. The initial states, positively and negatively charged polyenes in case of e-hR and low-lying excited singlets in case of ISC, are the eigenstates of the corresponding isolated species within the Pariser-Parr-Pople (PPP) model [13] with standard parameters and Ohno potentials [14] 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 polyene chain is given by [15]

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

where \( \hat{E}_{ij} = \sum_{\sigma} \hat{a}^\dagger_{i,\sigma} \hat{a}_{j,\sigma} \), \( \hat{n}_i = \sum_{\sigma} \hat{a}^\dagger_{i,\sigma} \hat{a}_{i,\sigma} \), and \( \hat{n}_i \) are the usual fermionic creation, annihilation, and number operators, respectively. \( \alpha_i \) and \( t_{ij} \) are, respectively, the site energies and hopping integrals, \( (ij) \) denotes the bonded pair, \( U_i \) denotes on-site correlations, and \( V_{ij} \) the intersite interactions. The Hamiltonian of the magnetic impurity is

$$H_P = \sum_{\sigma} \alpha_P \hat{a}_{i,\sigma}^\dagger \hat{a}_{i,\sigma} + \langle U_P/2 \rangle \hat{P} \hat{n}_P (\hat{n}_P - 1).$$

The total spin of the full system (impurity and the polyene moiety) 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 e-hR and ISC occur due to both
one-electron (CT pathways) and two-electron (exchange pathways) interactions [16,17] between the impurity and the polymer chain, schematically shown in fig. 1(c). Both these pathways are incorporated through the interaction Hamiltonian,

$$H_{int} = \sum_{ij} t_{ij}^e \hat{E}_{ij} + \sum_{ip} t_{ip}^e \hat{E}_{ip} + \sum_{ip} t_{ip}^e \hat{E}_{ip}$$

$$+ \frac{1}{2} \sum_{ijkl} (|J|/|k|) \hat{E}_{ij} \hat{E}_{kl} + |J|/|I| \hat{E}_{II} \hat{E}_{II}$$

$$+ \frac{1}{2} \sum_{pp'} mn (|p|/|m|) \hat{E}_{pp'} E_{mn} + |p|/|n| \hat{E}_{pm} \hat{E}_{p'n}),$$

where $t_{ij}^e$ is the one-electron transfer integral giving rise to the CT process and $|J|/|k|$ is the two-electron integral in charge cloud notation. Upper-case $I$ and $J$ correspond to orbitals on the second chain, $p$ and $p'$ correspond to orbitals on PM and indices $m$ and $n$ in the last summation run over orbitals on both chains. Terms involving upper-case indices in eq. (2) will occur only in e-hR process; in ISC these will be absent as only one polyene unit is involved in the latter studies.

Wave packet propagation technique is employed to study both the electronic processes involving the polymer system 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

$$\Psi_{e-hR}(0) = \frac{1}{\sqrt{6}} \begin{pmatrix} 1/2 & -1/2 \end{pmatrix}_{M^+} \otimes \begin{pmatrix} 1/2 & 1 \end{pmatrix}_{M^-} \otimes \begin{pmatrix} 1/2 & 1 \end{pmatrix}_{PM}$$

$$+ \frac{1}{\sqrt{6}} \begin{pmatrix} 1/2 & 1 \end{pmatrix}_{M^+} \otimes \begin{pmatrix} 1/2 & 1 \end{pmatrix}_{M^-} \otimes \begin{pmatrix} 1/2 & 1 \end{pmatrix}_{PM}$$

$$- \frac{2}{\sqrt{6}} \begin{pmatrix} 1/2 & 1 \end{pmatrix}_{M^+} \otimes \begin{pmatrix} 1/2 & 1 \end{pmatrix}_{M^-} \otimes \begin{pmatrix} 1/2 & 1 \end{pmatrix}_{PM}.$$  

(3)

All states are labeled by the spin quantum numbers $S$ and $M_s$. $|1/2, -1/2\rangle_{M^+}$ 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 by the time-dependent Schrödinger equation using the multistep differencing scheme (MSD) [18], with the total Hamiltonian given by $H_{M^+}^{PP} + H_{M^-}^{PP} + H_{PM} + H_{int}$. The evolved state, $\Psi_{e-hR}(t)$, is then projected onto 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 $|\langle \Psi_{e-hR}(0) | \langle \Psi_{e-hR}(t) \rangle |^2$. 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 [19]. The time-integrated yield of the triplet/singlet channel, $I_{T/S} \equiv \sum_{m} \int_{T_m}^{S_m} P_{T_m/S_m}(t) dt$, is thus a measure of the phosphorescence/fluorescence intensity in EL measurements.

To model the ISC process, we construct the initial state as the direct product of the singlet excited state of the molecule $(S_n)$ and PM which is given by, $\Psi_{ISC}(0) = |0, 0\rangle_n \otimes |1/2, -1/2\rangle_{PM}$, where $|0, 0\rangle_n$ is the $n$-th excited singlet state of the polyene expressed as linear combination of singlet VB functions and $|1/2, 1/2\rangle_{PM}$ is the $S = 1/2$ and $M_s = 1/2$ state of the PM. The initial state is time evolved as described previously for e-hR process using the total Hamiltonian given by, $H = H_{PP}^{PP} + H_{PM} + H_{int}$.

The evolved state ($\Psi_{ISC}(t)$) is then projected on to the direct product of the desired triplet eigen-states and the impurity state ($\Psi_{T_m,PM}$), keeping the total spin of the system conserved. The phosphorescence intensity in this process is taken to be proportional to the time-integrated triplet yield given by $\sum_{m} \int_{T_m}^{S_m} |\langle \Psi_{ISC}(t) | \Psi_{T_m,PM} \rangle|^2 dt$.

**Results.** — All EL and PL spectra have been normalized to the 0–0 vibronic peak. Since this work compares the relative intensity of the low-energy emission to the emission from singlet excitons, measuring absolute luminescence is not essential. Figure 1(b) compares the EL spectra of two PF2/6 LEDs prepared under ambient condition and N2 atmosphere. The intensity of green emission at 514 nm is substantially higher for the device prepared in N2. The device efficiencies were not optimized; turn-on voltages for all devices were ~5–6 V, as shown in fig. 1(d). Details of current-voltage characteristics in PF2/6 diodes are found in ref. [12]. Two batches of PF2/6 were used in this study. Figure 2 represents the EL and PL spectra (with PMs) utilizing the slightly higher-molecular-weight sample compared to fig. 1.

Figures 2(a) and (b) show the EL and PL spectra from Pd complex incorporated PF2/6 devices fabricated under N2 and ambient atmosphere, respectively. Figure 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-molecular-weight sample is lower than the low-molecular-weight sample (fig. 1(b)) in N2 atmosphere, all devices prepared under O2 atmosphere unambiguously have reduced green emission. The intensity of the green emission is much lower in the PL spectrum compared to the EL spectrum in both the environments. If the emission was due to oxidative defects, one would expect the devices prepared in air to show higher green emission 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
Incorporation of PMs quench the PL emission in both N\textsubscript{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 \textit{N}\textsubscript{2} and ambient conditions compared to as-is PF2/6 LEDs. The 514 nm EL emission is significantly higher for the N\textsubscript{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 [20].

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 for the N\textsubscript{2} devices (fig. 2(c)). The EL spectra of Cu(II)-incorporated PF2/6 LEDs in both N\textsubscript{2} and ambient atmosphere are shown in fig. 2(c). The intensity of 514 nm emission is slightly reduced for devices fabricated in O\textsubscript{2}.

Our experimental results are corroborated by the theory very well. The singlet-to-triplet state conversion by ISC pathway in the presence of paramagnetic metal is modeled for polyenes of different sizes; only the octatetraene results are presented in table 1. In addition to triplet yields through ISC process, we also present in table 1 the yield of singlet and triplet states for butadiene in e-hR process both in the presence and in the absence of PM. The polyene chains are modeled using standard PPP parameters for carbon [15]. The parameters for PM depend on the choice of number of orbitals on PM. The PM is modeled using either one or two d-orbitals with the Hubbard potential, \textit{U}=8.0\textsubscript{eV}, \textit{\alpha}_{P} varying between 2.0\textsubscript{eV} to 5.0\textsubscript{eV}, bond-bond repulsion integrals varying the PM and polyene orbitals is fixed at \sim 0.5\textsubscript{eV} for the nearest neighbor pairs and \textit{t}′ for nearest neighbor is fixed at \sim 0.2\textsubscript{eV}. These parameters are consistent with photo-emission spectroscopy data [21] for the d block metals whose d-orbital energies are 3 to 5 eV above the carbon 2p orbital energy. In ISC process the PM is placed at 4.0\textsubscript{Å} away from the center of the polyene chain along the perpendicular bisector whereas for the e-hR process, the butadiene units are placed end-on 3.0\textsubscript{Å} apart, and the paramagnetic site is located at 4.0\textsubscript{Å} on the perpendicular bisector of the full polyene system.

Since the triplet yields are only weakly dependent upon the site energies, we present the time-integrated yields of excited singlets and triplets for a single value of site energy, namely, \textit{\alpha}_{P}=5.0\textsubscript{eV} in table 1. In ISC process, the triplet yield is significantly higher when the unpaired electron is in a non-degenerate orbital. On the contrary, for an e-hR process a higher yield of triplets is observed when the unpaired electron resides in a pair of degenerate orbitals of the paramagnetic moiety. In the absence of PM the e-hR process yields more singlets than triplets. Moreover, the triplet yield in the presence of PM is much higher from e-hR process compared to the ISC pathway.

Table 1: Triplet yields (\textit{I}_T) in ISC and e-hR and singlet yields (\textit{I}_S) in e-hR for polyene. The superscripts 1 and 2 refer to number of orbitals on the PM atom. Superscript zero implies the absence of paramagnetic atom in the process.

| Pathways | Site energy of PM (eV) | \textit{I}_T | \textit{I}_S |
|----------|------------------------|--------------|--------------|
| ISC      | 5.0                    | 0.27\textsuperscript{1} | 0.003\textsuperscript{2} |
| e-hR     | 5.0                    | 0.09\textsuperscript{1} | 0.75\textsuperscript{1} |
| e-hR     | –                      | 1.28\textsuperscript{2} | 0.52\textsuperscript{2} |
| e-hR     | –                      | 0.29\textsuperscript{0} | 0.94\textsuperscript{0} |
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. In fact we observe a small decrease in the PL emission intensity since Pd and Cu quench triplets [22]. 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 O₂ which we attribute to the observed low intensity of green emission in samples prepared under ambient conditions with or without metal centers.

Discussion. – 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 triplets 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 the green emission could have occurred 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 [23]; our work clearly shows a large cross-section of triplets in the ch-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 N₂ atmosphere and ambient conditions with different transition metal and ion dopants. In addition, our theoretical studies of ISC and electron-hole recombination processes in the presence and absence of PMs as well as triplet state quenching by O₂ reinforces the experimental results. 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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