

# Photoluminescence Quenching in blends with Poly(3-hexylthiophene) and Fullerene/Non-fullerene Acceptors

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Md. Nasir Uddin<sup>1</sup>, Rafiqul Islam<sup>2</sup>, Muhibur Rahman<sup>3</sup>, Md. Mohibul Alam<sup>4</sup> and Nazia Chawdhury<sup>3\*</sup>

<sup>1</sup>Department of Physics, Mawlana Bhashani Science and Technology University, Tangail-1902, Bangladesh

<sup>2</sup>Department of Electrical and Electronic Engineering, Leading University, Sylhet-3112, Bangladesh

<sup>3</sup>Department of Physics, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh

<sup>4</sup>Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh

\*Corresponding Author's Email: nc-phy@sust.edu

## Abstract

Photogenerated charge transfer behavior from a p-type poly(3-hexylthiophene) (P3HT) donor material to an n-type fullerene and non-fullerene acceptor materials have been studied in blend solution with the help of photoluminescence (PL) quenching. The PL spectra were studied using two different excitation sources. The small gap fullerene-ethyl nipecotate and phenyl-C61-butyric acid methyl ester (PCBM) are fullerene-based and poly naphthalene-bithiophene (N2200) is a non-fullerene-based n-type acceptor material used in this research work. Observation shows that the P3HT:N2200 blend with a weight ratio of 1:0.07 in solution results in an efficient photogenerated charge transfer from P3HT to N2200.

**Keywords:** Bulk heterojunction; Exciton; Photoinduced carriers; Photoluminescence quenching.

## 1. Introduction

The delocalized  $\pi$ -electrons in  $\pi$ -conjugated polymers have their unique optical and electronic properties. These unique physical properties of the polymer result due to the rigid and co-planar conjugated chains in their chemical structure [1-3]. Conjugated polymers become promising materials in optoelectronic applications due to these physical properties in combination with lightweight, mechanical flexibility, and cost-effective low-temperature processing of the materials. Organic light emitting diodes (OLEDs), thin-film transistors, organic solar cells (OSCs) and many chemical sensors have been developed based on these materials [4-7]. Photoluminescence (PL) measurements of conducting polymers are used in data-storage devices and conductance switching applications [8], and to read the memory state for storage devices [9]. PL quenching is used in biomedical science in gas sensing and DNA/RNA detection [10,11]. Moreover, different types of molecular interactions such as molecular rearrangements, ground-state complex formation, excited state reactions, and energy transfer have been studied with the help of PL quenching [12]. A highly fluorescent conducting polymer poly(3-hexylthiophene) (P3HT) is used as the p-type electron donor in bulk heterojunction (BHJ) based organic solar

cell fabrication with a recorded power conversion efficiency of up to 5% [13-15]. Pristine fullerenes and their derivatives are used as promising acceptor materials in organic electronic device fabrication [16,17]. Among fullerene-based materials phenyl-C61-butyric acid methyl ester (PCBM) is widely used as an n-type acceptor in organic optoelectronic devices [18,19]. Small gap fullerene-ethyl nipecotate is another fullerene-based n-type acceptor material. In organic electronics, nowadays, blends of polymer:non-fullerene BHJ structures are also widely studied along with the blend of polymer: fullerene. The advantages of using a non-fullerene acceptor are its higher optical absorption, tunable chemical structure and lower cost compared with fullerene molecules [20]. As a non-fullerene acceptor material, the electrical and optical properties of poly naphthalene-bithiophene (N2200) are studying in BHJ structures [21] and are widely used as an n-type acceptor material for organic electronic device fabrication [22,23].

The photoluminescence quenching or PL intensity decay is the indication of photo-generated charge transfer from donor to acceptor material [24]. Goutam and his research team demonstrated that PL quenching increases by the addition of multiwalled carbon nanotube with P3HT polymer [25]. Recently Anefnaf

et al. studied the PL measurements of P3HT:PCBM in thin film and they reported that PL intensity quenches with an increase in PCBM. This quenching suggests that the transfer of photoinduced carriers from P3HT to PCBM increases with an increase in the amount of PCBM [26]. Similar studies have been shown by

Wahedd et al. where they reported that PL intensity quenches as the amount of PCBM acceptor increases into the blend of P3HT:PCBM [27]. Generally, non-fullerene acceptors exhibit strong absorption in the visible and NIR region. Yen et al. theoretically reported that the energy levels of non-fullerene acceptors properly matches with the donor energy levels for achieving efficient charge separation [28]. Anderson and his research team concluded that the blend of P3HT:N2200 exhibits good photochemical stability that can be used to analyze the effect of light soaking on electronic properties [29]. The solar cell device performance depends on dissociation, transport and collection of charge carriers that lead to better or poor

device efficiency. Therefore, photo-induced charge carriers are very essential for an efficient photovoltaic device. In this research work, PL quenching of P3HT: Fullerene and P3HT: Non-fullerene blend solution were studied to understand the charge transfer behavior from a donor region to an acceptor region.

## 2. Experimental

### 2.1 Materials

Poly(3-hexylthiophene-2,5-diyl) (P3HT) with molecular weight, MW~ 20,000-70,000 g/mol was purchased from 'Alpha Aesar', and small gap fullerene-ethyl nipecotate (MW~ 2100 g/mol) and phenyl-C61-butyric acid methyl ester (PCBM) (MW~ 910.88 g/mol) were purchased from 'Sigma-Aldrich'. Polynaphthalene bithiophene (N2200) polymer was used as received from Organic Optoelectronic Materials Laboratory, Department of Chemistry, Korea University. In this experiment, all the polymers were used without any further modifications.

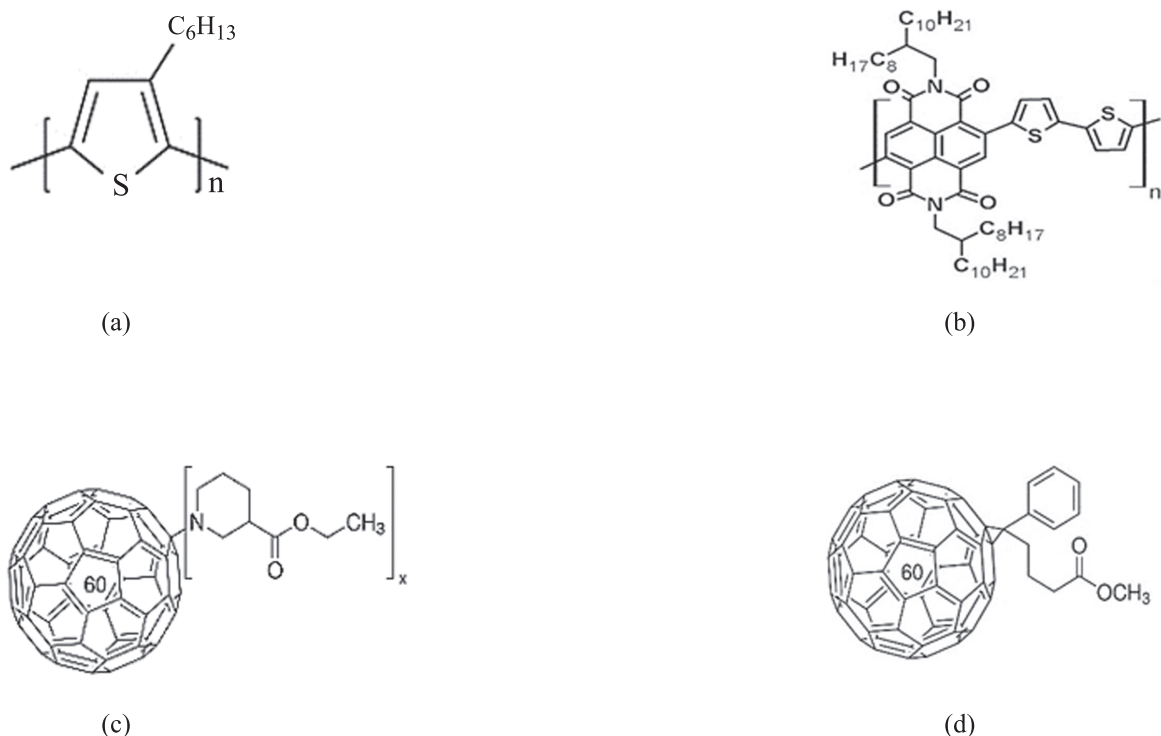


Figure 1. Schematic representation of (a) P3HT polymer (b) N2200 polymer (c) Fullerene-EN (small gap fullerene-ethyl nipecotate) and (d) PCBM molecule.

## 2.2 Sample preparation

For UV-visible absorption and PL spectroscopy, 1 mg of P3HT polymer was dissolved in a 4 ml chloroform solvent. Then the solution was diluted by adding an appropriate amount of solvent to make the concentration 0.025 mg/ml. Similarly, for PL measurements using Ar<sup>+</sup> laser, separate solutions of P3HT, N2200, Fullerene-EN and PCBM were prepared in chloroform solvent with a concentration of 0.2 mg/ml. All the solutions were diluted by the addition of appropriate amount of solvent. The blend solutions of P3HT:Acceptors were prepared using a micropipette with different P3HT-acceptor weight ratios. The amount of P3HT in the ratio was the same for all the solutions. Solutions of P3HT: N2200 with the weight ratios of 1:0, 1:0.5, 1:2, and 1:3 were prepared for PL measurement using a spectrofluorophotometer. While for the PL measurements using Ar<sup>+</sup> laser, the solutions of P3HT:N2200 with the weight ratios of 1:0.00, 1:0.01, 1:0.02, 1:0.04, 1:0.05, 1:0.06, and 1:0.07 were used. In similar experiments, the blends of P3HT: Fullerene-EN with weight ratios of 1:0, 1:0.12, 1:0.25, 1:0.37, and 1:0.50, and the blends of P3HT: PCBM with weight ratios of 1:0.00, 1:0.25, 1:0.31, 1:0.37, and 1:0.43 were used.

## 2.3 Experimental

A UV-VIS spectrophotometer (Shimadzu, UV-1800 PC) was used to measure UV-visible absorption spectroscopy. Photoluminescence (PL) measurements were studied using spectrofluorophotometer (Shimadzu RF- 5301 PC). A 514 nm (2.41 eV) line of an argon ion (Ar<sup>+</sup>) laser was used to excite the blends. The laser power was set to 21.1 mW. A Neutral-density (ND) filter was used to control the intensity of the laser beam and a beam splitter was used for reference intensity detection. The PL signals were measured using a spectrograph connected to a charged coupled device (CCD) (Newport ORIEL 77400). A LineSpec Basic software was used to save the experimental data. Laser power, experimental geometry and acquisition time were kept same during the measurements. The acquisition time was kept as minimum as possible to avoid sample degradation. All the measurements were done at the laboratory environment. Therefore, the sample were exposed to air. Jin et al. reported that during the measurements of few hours' exposure to air, no chemical oxidation of P3HT or PCBM occurred in the solutions [30]. Therefore, we expect no PL intensity decay due to chemical degradation of the sample in this short time.

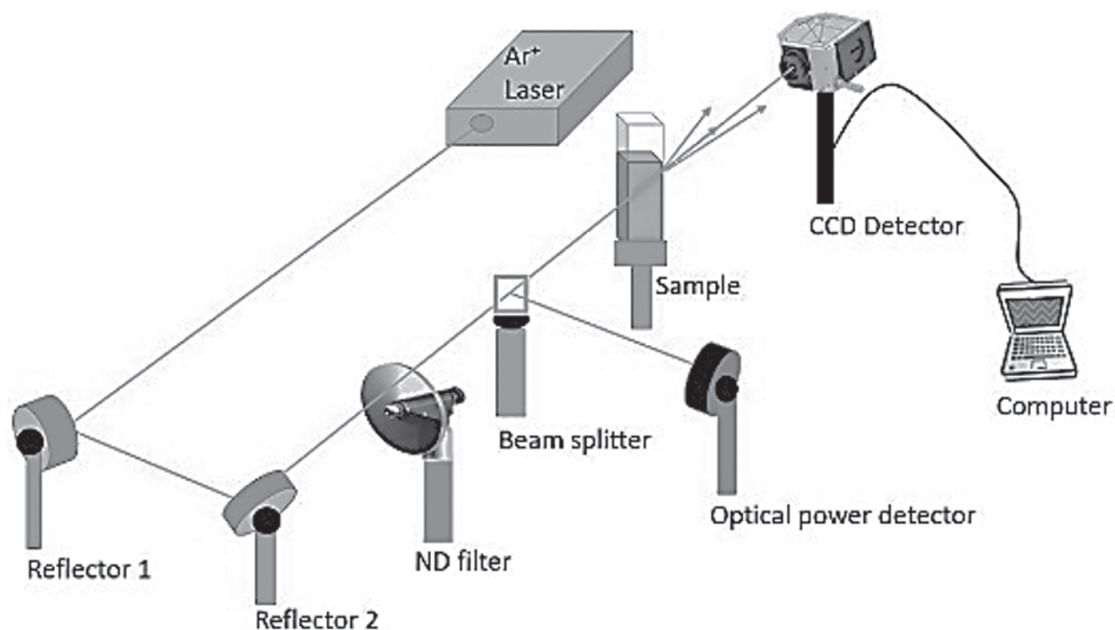


Figure 2. Experimental setup for photoluminescence measurements using Ar<sup>+</sup> laser and CCD detector.

### 3. Results and discussion

The photoluminescence (PL) spectroscopy of the blend of P3HT with fullerene and non-fullerene acceptors with different weight ratios of the acceptor materials were studied by two different techniques (i) using spectrofluorometer and (ii) using a 514 nm line of an Ar<sup>+</sup> laser as excitation sources. Optical absorption and PL spectra of P3HT polymer in solution is shown in figure 3 as a function of energy (eV). It has been observed that the maximum absorbed energy for P3HT polymer is 2.78 eV whereas the maximum PL intensity is at 2.03 eV. The PL spectrum is Stokes shifted by energy 0.75 eV. The laser line at 2.41 eV is also observed in figure 3. Figure 4 shows the concentration dependency of acceptor material on PL spectra of P3HT:N2200, P3HT:Fullerene-EN and P3HT:PCBM blend. It has been observed that the PL intensity decreases or quenches gradually as the amount of acceptor materials increases in the P3HT:N2200, P3HT:Fullerene-EN and P3HT:PCBM blend solutions.

The results in figure 4(a) shows a PL peak at energy around 2.2 eV for P3HT:N2200 blend solution with maximum decrease in PL intensity by 40 a.u. (arbitrary unit) for the change in acceptor material from 1:0.0 to 1:3.0 in the blend ratio. Here we do not observe any vibronic structures. However, excitation with a laser line shows structured electronic transitions. Figures 4(b), 4(c), and 4(d) display the appearance of two peaks at different energies that are attributed to the transitions from lower singlet excited state (S1) to different vibronic states of ground states (S0). After excitation to an upper vibronic state, the nuclear coordinates are not in their equilibrium configuration for the new electronic state, and hence radiationless relaxation between the vibrational states occur. After relaxing to the lowest vibrational state,  $n=0$  of the excited state, the excitation return to the different vibronic state of the ground state by emitting

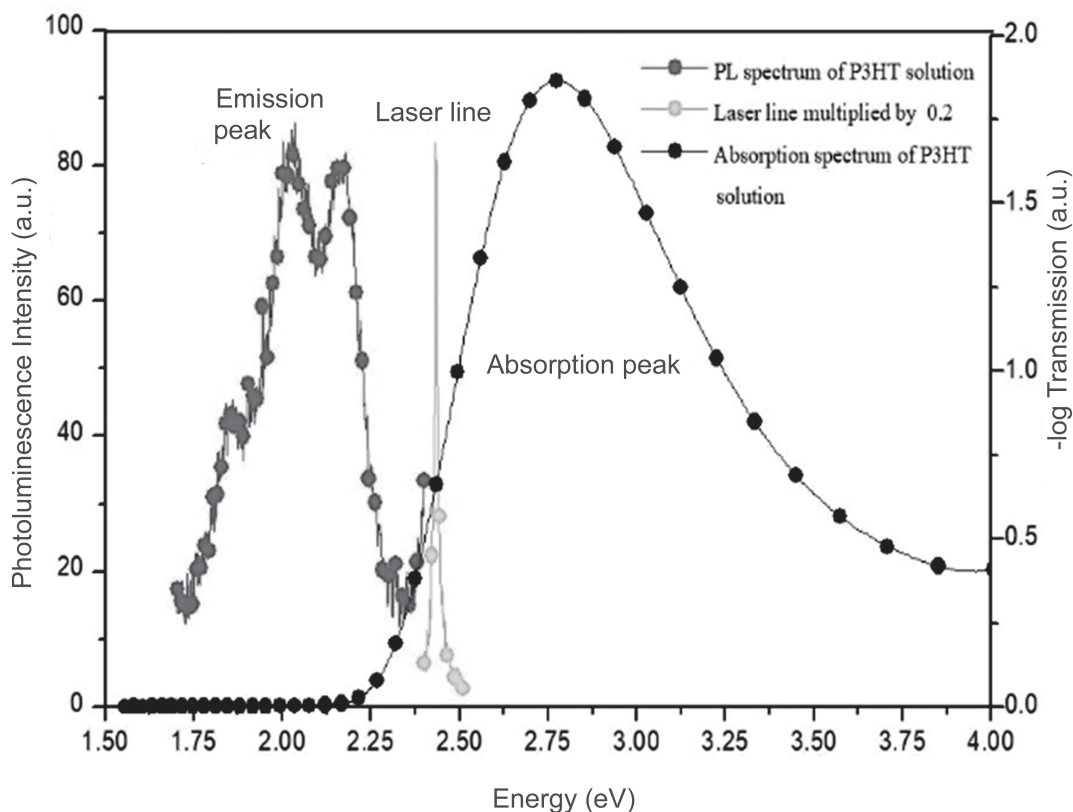
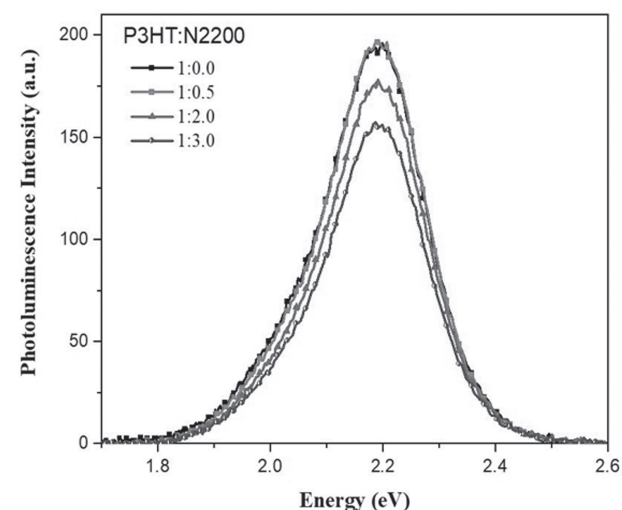


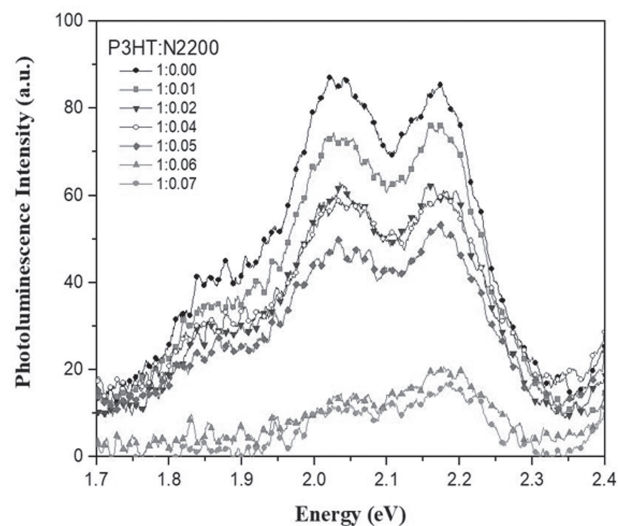
Figure 3. PL and absorption spectra of P3HT polymer in solution.

a photon [31]. Comparing the results shown in figure 4(b), (c) and (d), we find that PL intensity decreases significantly with increasing acceptor in P3HT:N2200 blend. We find that more amount of acceptor materials were needed to decrease comparable amount of the PL intensity for P3HT:PCBM and P3HT:Fullerene-EN. These results indicate that poor charge transfer occurs from P3HT polymer to PCBM and Fullerene-EN.

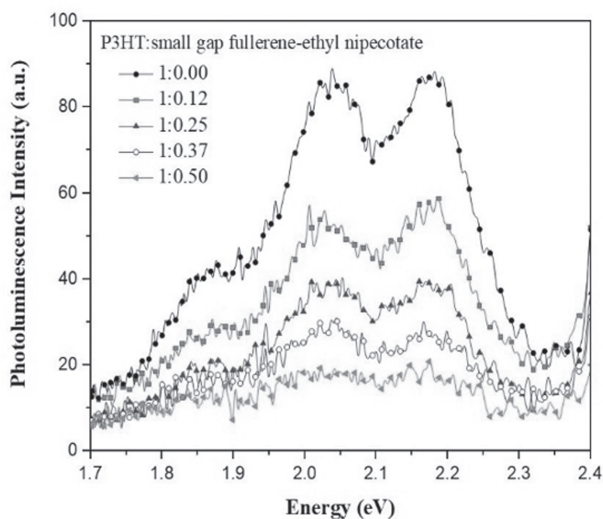
In organic photovoltaic devices, photo generated exciton (bound electron-hole pair) in P3HT polymer diffuses towards the P3HT:Acceptor interface. An efficient electron transfer process results in the dissociation of this exciton into free electron and hole at the interface leading to generation of photocurrent.



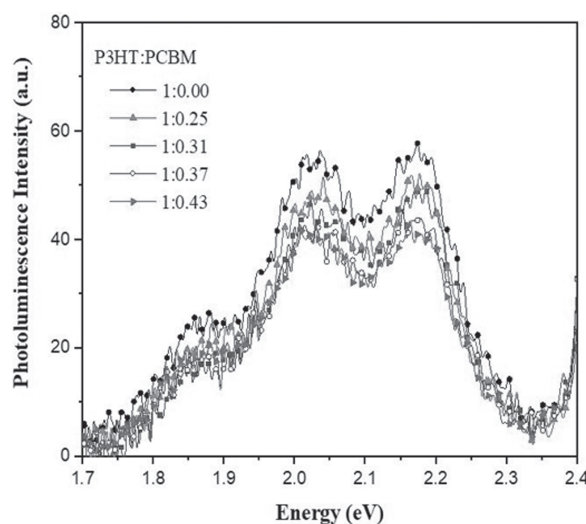
(a)



(b)



(c)



(d)

Figure 4. PL emission spectra of (a) P3HT:N2200 with 450 nm excitation from using spectrofluorometer, (b) P3HT:N2200, (c) P3HT: Fullerene-EN, and (d) P3HT:PCBM using 514 nm wavelength and 21.1 mW power Ar<sup>+</sup> laser excitation.

The molecular orbital energy of P3HT and acceptor material is a subject of great importance for the process of efficient electron transfer. Ping-Tsung Huang et al. experimentally reported that an efficient charge transfer or the probability of charge transfer increases as the amount of PCBM increases in the blend of P3HT:PCBM solution which is confirmed by the quenching of PL intensity [32]. Julia Yu Mayorova and co-workers found that the PL intensity decay increased when fullerene or its derivatives were mixed with conjugated semiconducting polymers [33]. They also conclude that, in polymer:fullerene blends, PL quenching allows efficient charge separation resulting in better power conversion efficiency of organic solar cells. A parameter that describes the charge transfer or the energy transfer behavior from donor to acceptor material is the PL quenching parameter ( $q$ ), defined as [32].

$$q = \frac{I_{\text{donor}} - I_{\text{donor:acceptor blend}}}{I_{\text{donor}}} \times 100\% \quad (1)$$

Where,  $I_{\text{donor}}$  and  $I_{\text{donor:acceptor blend}}$  are the PL intensity of donor and donor:acceptor blend solution. The maximum value of ' $q$ ' refers to the efficient electron transfer process from donor to acceptor material. Table 1 and table 2 show the calculated quenching parameters,  $q$ , from the experimental data of the blends. The blend of P3HT:N2200 polymers with a weight ratio of 1:0.07 shows better quenching with the  $q$  value 85 %. Whereas, the maximum  $q$  values for the blend of P3HT:Fullerene-EN and P3HT:PCBM are 79.9 % and 31.2 % respectively. In the case of P3HT:N2200 blend, the generated exciton at the donor-acceptor interface efficiently dissociated into free carriers. Facchetti et al. reported that non-fullerene acceptor materials show higher optical absorption and tunable chemical structure compared to the fullerene molecules [34]. This tunability of the LUMO and HOMO energy levels of the N2200 acceptor matches the LUMO and HOMO energy levels of the P3HT donor. This explains the reason for the efficient exciton dissociation or charge separation from P3HT to N2200 [35-36].

**Table 1.** Photoluminescence quenching parameter ( $q$ ) in blend with P3HT and at different weight ratio of N2200 polymer measured by spectrofluorometer.

P3HT:N2200	1:0.0	1:0.5	1:2.0	1:3.0
$q$ (%)	0.0	0.0	9.2	19.2

**Table 2.** Photoluminescence quenching parameter ( $q$ ) in blends with P3HT and at different weight ratio of N2200, Fullerene-EN and PCBM by Ar+ laser as source of excitation.

P3HT:N2200	1:0.0	1:0.01	1:0.02	1:0.04	1:0.05	1:0.06	1:0.07
$q$ (%)	0.0	15.9	28.9	37.7	44.9	85.0	85.0
P3HT: Fullerene-EN	1:0.0	1:0.12	1:0.25	1:0.37	1:0.50		
$q$ (%)	0.0	36.6	53.3	68.3	79.9		
P3HT:PCBM	1:0.0	1:0.25	1:0.31	1:0.37	1:0.43		
$q$ (%)	0.0	12.0	12.0	26.2	31.2		

## Conclusion

We have shown that, the photoluminescence intensity decreases with the increase of acceptor materials in the P3HT:N2200, P3HT:Fullerene-EN, and P3HT:PCBM blend solutions in order to investigate the charge transfer behavior from a donor region to an acceptor region. The experimental result concludes that the photoluminescence quenching or PL intensity decay in P3HT:N2200 solution is most efficient compared to the blends with fullerene derivatives. Efficient photoinduced electron transfer occurs from P3HT to N2200 polymer is essential for bulk heterojunction (BHJ) photovoltaic devices. Here, the charge transfer behavior becomes more effective at a higher concentration solution of N2200 or a shorter distance between P3HT and N2200. Comparison of PCBM and small gap fullerene-ethyl nipecotate BHJ structures, it has been observed that the latter one shows better charge transfer behavior. Due to this property of the material, we suggest that small gap fullerene-ethyl nipecotate can be used as an n-type acceptor material in fullerene based organic electronic device fabrication.

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