

Fluorescence Quenching of Substituted Polyperylene with Functionalized Polythiophenes

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Abstract The present investigation focuses the influence of polythiophene i) containing hetero aromatic structures and ii) containing mesogenic groups towards the photoluminescence properties of substituted polyperylene (PPE). The structural contribution towards the optical properties was individually discussed. The photoluminescence of PPE was quenched to the maximum level (30%) when it was blended with polythiophene with mesogenic groups containing longer alkyl spacer. Results of the same blend in solid-state shows 85% of PL quenching.

Keywords Photoluminescence · Perylene derivatives · Polythiophene · Polymer blends

Introduction

π -Conjugated semiconducting polymers are molecular analogs of inorganic semiconductors, which are having the ability to prepare junctions with well-defined electronic properties. These materials are the prominent materials used for the fabrication of various organic electronic devices [1–2] such as light emitting diodes [3–4], photovoltaic devices [5–6] etc. Among various conjugated polymers, polythiophenes have received considerable attention due to their excellent electrical characteristics [7–9]. Moreover

polythiophene family is well known for its environmental stability, melt and solution processability and versatile synthesis that allows us to have a significant control over optical and electronic properties [10].

The underlying principle in organic semiconductors by photo excitation is that singlet-excitons which are created [11] likely to dissociate into free charges at donor/acceptor interfaces. Exciton dissociation is known to be efficient at the interface between materials of different ionization potentials and electron affinity. Recently, photovoltaic devices based on donor-acceptor blends of conjugated polymers that form an interpenetrating network have been shown to be highly efficient [12]. This approach was used to enhance the efficiency of organic solar cells using fullerene (C_{60}) derivatives as electron acceptor in hetero junction and blend device [13–16].

High oxygen sensitivity of fullerene offers a big hindrance towards its projected applications. It is important to note that C_{60} derivatives in general has a low absorption coefficient in the visible region of spectrum and hence provides a relatively small contribution to the photocurrent. Organic pigments of perylene family are good substitute of fullerene as n-type organic semiconductor with high electron mobility and least oxygen sensitivity [17].

Interpenetrating networks of a hexa benzocoronene derivative and a perylene compound show a much larger efficiency than samples containing two flat layers consisting of the same materials [18]. Rudino et al examined the morphological characteristics of perylene-doped phthalocyanine thin films and their photovoltaic effect [19]. The effect of fullerene (C_{60}) doping on photoelectric conversion using titanyl phthalocyanines and a perylene pigment, N,N' -dimethyl-3,4:9,10-perylene bis(dicarbodiimide) was investigated [20]. Photo carrier generation and photovoltaic effect have been systematically studied in single layer poly

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(3-alkylthiophene)(P3AT)- perylene hetero junction cells [21]. Zafer et al investigated *N, N'*-bis-2-(1-hydroxy-4-methylpentyl)-3, 4, 9, 10-perylene bis (dicarboximide) sensitized nanocrystalline TiO₂ with polythiophene hole conductors in solar cell applications [22] also studied the influence of the spacer alkyl chain length of perylene mono imide (PMI) dyes on the device performance in dye sensitized solar cells (DSSCs) [23].

The experimental observation of photo induced charge transfer between photo-excited state of a non-degenerate conjugated polymer to suitable acceptor by spectroscopic techniques stimulated the intensive research [24]. The photoluminescence is quenched by blending of a few percent of acceptor moiety with the strongly luminescent donor moiety and the steady state photoconductivity is increased in perylene-based system [25].

The present work focuses on the design of polythiophenes containing different functional groups (Fig. 1) and the detailed study of its mutual influence on photoluminescence quenching of substituted polyperylene (PPE) (Fig. 1(g)). Compounds in Fig. 1a–c namely; poly benzo thia-diazolidene-3-thiophene (BTDT), poly (6-ethoxy benzothiazolidene)-3-thiophene (AZEBT), poly (benzimidazolidene-3-thiophene) (BIT) respectively were designed in such a way, the hetero aromatic side chain may enhance the electronegativity and also may aid for electron transfer. Since the rigid rod polymers have a controlled packing which in turn improve the performance of the devices. Polythiophenes having mesogenic side chains with variation in linkage and spacer length has been used in this investigation (Fig. 1(d–f) (1d. poly (3-ethoxy benzoyloxy aniline) thiophene (N2)), 1e. poly (3- decyloxy benzoyloxy

aniline) thiophene); 1f. poly (3-decyloxy phenoxy amino benzoate) thiophene). Substituted polyperylene was blended with the above compounds and the influence of blend composition on the photo luminescence is studied in detail with the view to get the material with enhanced properties for Optoelectronics.

Materials and methods

Polythiophenes containing hetero aromatic side chains were synthesized by using the following general procedure. The corresponding amines, dissolved in ethanol were reacted with thiophene-3-carboxaldehyde in the presence of catalytic amount of acetic acid. The mixture was refluxed for an hour and the resulting solid was filtered and washed with ethanol. The compound was purified by recrystallisation [26]. Thiophenes with side chain bearing mesogen and spacer groups are synthesized using the procedure reported in the work published by Narasimhaswamy et al [27].

Preparation of Alkoxy benzoyloxy aniline (N2 and N10)

4-hydroxy benzoic acid was reacted with alkyl bromide (RBr, R=2,10) in presence of potassium hydroxide (KOH) in ethanol. The corresponding acid chloride was prepared using SOCl₂ in Dimethyl Formamide(DMF). Then it is coupled with 4-hydroxy nitro benzene in triethyl amine (TEA) and Methyl ethyl ketone (MEK) medium. The resulting nitro compound was reduced in ethanol medium using Tin (II) chloride. The schiff bases of the amines were

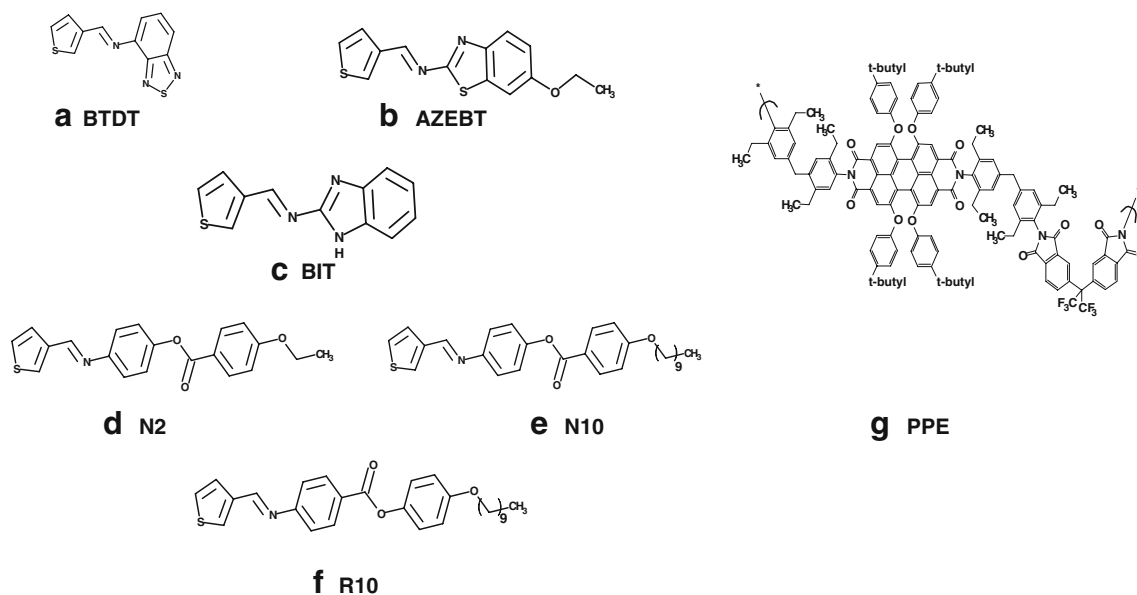


Fig. 1 a–c Representative repeating units of the thiophene containing heteroaromatic sidechain; d–f Representative repeating units of the thiophene containing mesogenic groups g substituted polyperylene

dissolved with absolute ethanol and mixed with thiophene carboxaldehyde. Catalytic quantity of glacial acetic acid was added to the reaction mixture and contents were refluxed. The solid crystallized out on cooling the reaction mixture was purified by recrystallization.

Preparation of Alkoxy phenoxy amino benzoates (R10)

Preparation of Alkoxy phenoxy amino benzoates (R10) compounds were synthesized by reacting 4-Hydroxy phenol with alkyl bromide (RBr, R=10) in ethanolic KOH and it was coupled with 4-nitro benzoyl chloride in TEA/MEK. The resulting compound was reduced using SnCl₂. The schiff bases of the amines were prepared by adopting the procedure mentioned above.

The polymer of the above monomers was obtained [M_w around 17,000], using electrochemical polymerization [26]. The reaction was carried out in acetonitrile containing tetra butyl ammonium hexa fluoro phosphate (TBAPF₆) as the electrolyte. Current density for the polymerization reaction was 2 mA/cm² and the reaction was performed for 3 hrs with the above current density. Dedoping of the formed polymers was carried out for about 30 min. by reversing the polarity. The time of reaction and dedoping were fixed on the basis of applied current. Substituted polyperylene was obtained from the research group of University of Bayreuth. Solvents like chloroform, ethanol, and acetonitrile were purchased from Aldrich and were used without further purification.

Stock solutions of poly thiophene and substituted poly perylene were prepared by dissolving 1mg of polymer in

10 ml of chloroform. Solution blends of polymers with PPE were prepared by mixing 1ml of stock solution of PPE with varied volumes of polymer stock solution. Total volume of the blend solution (10 ml) was kept constant by adding appropriate volume of solvent. Similar procedure was adopted for the remaining blends. The UV spectra of the blends were recorded using CARY 50 Bio UV visible spectrophotometer while CARY eclipse spectro fluorimeter containing solid sample holder was use to record the fluorescence. Since the obtained spectrum is broad, 'Spec-viewer' software from ACD Labs is used to deconvolute the spectra. The peaks were identified from first and second derivative curves of the original spectra.

Results and discussion

π -donor /acceptor considered to be a promising candidate in organic electronics both in photovoltaic and in display technologies. In this direction, mutual interactions and influence on optical properties in donor and acceptor in the form of blend is of commercial importance. In the present study, influence of six different functionalized polythiophene (Fig. 1) on photoluminescence properties of PPE was investigated.

Effect of concentration of polythiophene containing hetero aromatic side chain on PPE emission

In Table 1, the effect of concentration of the BTDT polymer on the photoluminescence of PPE is presented for two

Table 1 Effect of BTDT polymer concentration on PPE emission intensity

| | PPE:BTDT | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) |
|-----------------|----------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|
| BTDT | | | | | | | | | |
| λ_{exc} | 545 nm | | | | | | | | |
| λ_{emi} | | 615 nm | | 636 nm | | 654 nm | | 674 nm | |
| A6 | 100–0 | 185.00 | 100.00 | 88.20 | 100.00 | 37.12 | 100.00 | 21.00 | 100.00 |
| A1 | 90–10 | 205.00 | 110.81 | 97.02 | 110.00 | 40.96 | 110.34 | 24.00 | 114.29 |
| A2 | 80–20 | 201.25 | 108.78 | 98.28 | 111.43 | 42.24 | 113.79 | 22.50 | 107.14 |
| A3 | 50–50 | 210.00 | 113.51 | 98.28 | 111.43 | 40.96 | 110.34 | 24.00 | 114.29 |
| A4 | 20–80 | 212.50 | 114.86 | 104.58 | 118.57 | 44.80 | 120.69 | 25.50 | 121.43 |
| A5 | 10–90 | 207.50 | 112.16 | 97.02 | 110.00 | 40.96 | 110.34 | 22.50 | 107.14 |
| BTDT | | | | | | | | | |
| λ_{exc} | 588 nm | | | | | | | | |
| λ_{emi} | | 613 nm | | 627 nm | | 644 nm | | 664 nm | |
| A6 | 100–0 | 556.00 | 100.00 | 388.02 | 100.00 | 158.98 | 100.00 | 74.88 | 100.00 |
| A1 | 90–10 | 627.44 | 110.48 | 429.43 | 110.67 | 173.95 | 109.42 | 80.73 | 107.81 |
| A2 | 80–20 | 610.08 | 107.42 | 417.60 | 107.62 | 170.50 | 107.25 | 79.56 | 106.25 |
| A3 | 50–50 | 624.96 | 110.04 | 422.33 | 108.84 | 173.95 | 109.42 | 80.73 | 107.81 |
| A4 | 20–80 | 643.56 | 113.32 | 438.89 | 113.11 | 180.86 | 113.77 | 84.24 | 112.50 |
| A5 | 10–90 | 627.44 | 110.48 | 430.61 | 110.98 | 182.02 | 114.49 | 86.58 | 115.63 |

different intense wavelength values of poly perylene as excitation. For better understanding, Table 1 also shows the percentage of change with respect to the original PPE emission. With addition of 10% of BTDT, there is an increase in intensity of intense emission (613 nm). The intensity of other emissions also follow the same trend. Further addition of polymer in the blend does not show characteristic variation up to 20% BTDT in the blend. Further addition of polymer slightly increases the intensity of polymer emission. The same trend is obtained both for 545 nm and 588 nm excitation.

Addition of 10% of AZEBT polymer in the solution interestingly quenches the intensity of PPE (613 nm) for both 545 nm and 588 nm excitation (Table 2). Unlike BTDT, further addition of AZEBT polymer increases the emission intensity of poly perylene ranges. It is interesting to note, in contrast to BTDT, AZEBT contain a non-polar ethoxy terminal group in the side chain. Substituted poly perylene contain more number of non-polar t-butyl groups. Therefore it is probable that the more secondary interaction would have formed to make this as compatible blend. Because of good compatibility, there is an efficient quenching by AZEBT, whereas, BTDT contain rings with more electro-negativity. So comparably lower quenching efficiency is observed in these blends. Change in quantity of AZEBT with change in intensity is also characteristic and therefore, with the increase of AZEBT, the intensity of emission increases. It is also interesting to note that the increase in intensity characteristically (AZEBT) changes with high slope after 33% of polymer in the blend. It is observed that after initial quenching due to the addition of

polymer, about 60% of AZEBT is required to reach the comparable value of pure PPE.

Unlike AZEBT, addition of BIT does not modify the emission of PPE (Table 3). This can be understood due to the more polar nature of the side chain, which is similar to BTDT. Both BTDT and BIT contain rigid structures without additional functional groups in the hetero aromatic chain to enhance the interaction. Therefore it is probable for low variation in optical properties of PPE.

Effect of concentration of polythiophene containing mesogenic side chain on PPE emission

It is known that the rigid rod structures form into an ordered pattern in thin films as well as in solution. Rigid rod structures like polythiophenes containing mesogenic side chains were designed in order to understand the influence of orderliness on PL modification of PPE. In Table 4 the effect of concentration of N2 polymer (Fig. 1(d)) on fluorescence of PPE under 545 nm and 588 nm (Fig. 2) excitation is presented. It is amazing to note that the intense emission at 613 nm ($\lambda_{exc}=545$ nm) is increased by 40% by the small addition of 10% of N2 polymer (Fig. 2). Further addition of polymer in the blend initially increases the emission up to 20%. The PL intensity of PPE ($\lambda_{exc}=545$ nm) shows characteristic decrease by further addition of N2 polymer (slope=-0.315). It is interesting to note that at addition of 10% N2 polymer, the increase in intensity characteristically, decrease with emission intensity of lower wavelengths. For example, for 613 nm emission, the intensity reaches 40% to the original PPE intensity while

Table 2 Effect of AZEBT polymer concentration on PPE emission intensity

| | PPE: AZEBT | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) |
|-----------------|------------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|
| AZEBT | | | | | | | | | |
| λ_{exc} | 545 nm | | | | | | | | |
| λ_{emi} | | 612 nm | | 621 nm | | 635 nm | | 647 nm | |
| | 100–0 | 184.24 | 100.00 | 159.96 | 100.00 | 87.84 | 100.00 | 50.00 | 100.00 |
| | 90–10 | 165.44 | 89.80 | 143.22 | 89.53 | 76.86 | 87.50 | 42.00 | 84.00 |
| | 80–20 | 174.84 | 94.90 | 150.66 | 94.19 | 78.69 | 89.58 | 44.00 | 88.00 |
| | 66.5–33.5 | 172.96 | 93.88 | 145.08 | 90.70 | 76.86 | 87.50 | 46.00 | 92.00 |
| | 20–80 | 197.40 | 107.14 | 169.26 | 105.81 | 93.33 | 106.25 | 52.00 | 104.00 |
| | 10_90 | 203.04 | 110.20 | 172.98 | 108.14 | 95.16 | 108.33 | 56.00 | 112.00 |
| B-series | | | | | | | | | |
| λ_{exc} | 588 nm | | | | | | | | |
| λ_{emi} | | 613 nm | | 635 nm | | 648 nm | | 676 nm | |
| | 100–0 | 556.92 | 100.00 | 260.64 | 100.00 | 149.38 | 100.00 | 46.59 | 100.00 |
| | 90–10 | 464.10 | 83.33 | 224.44 | 86.11 | 124.16 | 83.12 | 39.94 | 85.71 |
| | 80–20 | 513.24 | 92.16 | 235.30 | 90.28 | 131.92 | 88.31 | 38.27 | 82.14 |
| | 66.5–33.5 | 504.14 | 90.52 | 244.35 | 93.75 | 126.10 | 84.42 | 39.94 | 85.71 |
| | 20–80 | 591.50 | 106.21 | 276.93 | 106.25 | 159.08 | 106.49 | 46.59 | 100.00 |
| | 10–90 | 596.96 | 107.19 | 295.03 | 113.19 | 157.14 | 105.19 | 46.59 | 100.00 |

Table 3 Effect of BIT polymer concentration on PPE emission intensity

| BIT | | PPE: BIT | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) |
|-----------------|--------|----------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|
| λ_{exc} | 545 nm | | | | | | | | | |
| λ_{emi} | | 613 nm | | | 625 nm | | 636 nm | | 646 nm | |
| | 100–0 | 185.00 | 100.00 | 143.00 | 100.00 | 88.00 | 100.00 | 50.00 | 100.00 | |
| | 90–10 | 181.00 | 97.84 | 136.00 | 95.10 | 83.00 | 94.32 | 49.00 | 98.00 | |
| | 80–20 | 184.00 | 99.46 | 138.00 | 96.50 | 85.00 | 96.59 | 52.00 | 104.00 | |
| | 72–28 | 186.00 | 100.54 | 140.00 | 97.90 | 86.00 | 97.73 | 53.00 | 106.00 | |
| | 67–33 | 187.00 | 101.08 | 142.00 | 99.30 | 87.00 | 98.86 | 54.00 | 108.00 | |
| | 63–37 | 195.00 | 105.41 | 146.00 | 102.10 | 89.00 | 101.14 | 56.00 | 112.00 | |
| | 55–45 | 193.00 | 104.32 | 144.00 | 100.70 | 84.00 | 95.45 | 53.00 | 106.00 | |
| | 50–50 | 190.00 | 102.70 | 140.00 | 97.90 | 84.00 | 95.45 | 50.00 | 100.00 | |
| | 20–80 | 189.00 | 102.16 | 139.00 | 97.20 | 88.00 | 100.00 | 48.00 | 96.00 | |
| | 15–95 | 185.00 | 100.00 | 149.00 | 104.20 | 90.00 | 102.27 | 54.00 | 108.00 | |
| BIT | | | | | | | | | | |
| λ_{exc} | 588 nm | | | | | | | | | |
| λ_{emi} | | 613 nm | | 628 nm | | 636 nm | | 645 nm | | |
| | 100–0 | 556.00 | 100.00 | 388.00 | 100.00 | 261.00 | 100.00 | 159.00 | 100.00 | |
| | 90–10 | 540.00 | 97.12 | 370.00 | 95.36 | 249.00 | 95.40 | 157.00 | 98.74 | |
| | 80–20 | 545.00 | 98.02 | 374.00 | 96.39 | 252.00 | 96.55 | 161.00 | 101.26 | |
| | 72–28 | 549.00 | 98.74 | 376.00 | 96.91 | 253.00 | 96.93 | 162.00 | 101.89 | |
| | 67–33 | 552.00 | 99.28 | 377.00 | 97.16 | 256.00 | 98.08 | 165.00 | 103.77 | |
| | 63–37 | 569.00 | 102.34 | 383.00 | 98.71 | 263.00 | 100.77 | 163.00 | 102.52 | |
| | 50–50 | 567.00 | 101.98 | 379.00 | 97.68 | 259.00 | 99.23 | 155.00 | 97.48 | |
| | 20–80 | 565.00 | 101.62 | 378.00 | 97.42 | 258.00 | 98.85 | 162.00 | 101.89 | |
| | 15–95 | 564.00 | 101.44 | 389.00 | 100.26 | 263.00 | 100.77 | 165.00 | 103.77 | |

Table 4 Effect of N2 polymer concentration on PPE emission intensity

| N2 | | PPE:N2 | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) |
|-----------------|--------|--------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|
| λ_{exc} | 545 nm | | | | | | | | | | | |
| λ_{emi} | | 613 nm | | | 627 nm | | 638 nm | | 651 nm | | 675 nm | |
| | 100–0 | 185.09 | 100.05 | 143.00 | 100.00 | 87.84 | 100.00 | 38.93 | 100.00 | 16.92 | 100.00 | |
| | 90–10 | 259.12 | 140.06 | 178.75 | 125.00 | 106.14 | 120.83 | 41.22 | 105.88 | 16.92 | 100.00 | |
| | 80–20 | 263.23 | 142.29 | 186.69 | 130.56 | 102.48 | 116.67 | 41.22 | 105.88 | 15.51 | 91.67 | |
| | 67–33 | 238.55 | 128.95 | 170.80 | 119.44 | 98.82 | 112.50 | 36.64 | 94.12 | 12.69 | 75.00 | |
| | 50–50 | 238.55 | 128.95 | 170.80 | 119.44 | 91.50 | 104.17 | 36.64 | 94.12 | 11.28 | 66.67 | |
| | 20–80 | 209.76 | 113.39 | 154.92 | 108.33 | 80.52 | 91.67 | 29.77 | 76.47 | 11.28 | 66.67 | |
| | 10–90 | 197.42 | 106.72 | 131.08 | 91.67 | 73.20 | 83.33 | 27.48 | 70.59 | 9.87 | 58.33 | |
| N2 | | | | | | | | | | | | |
| λ_{exc} | 588 nm | | | | | | | | | | | |
| λ_{emi} | | 613 nm | | 627 nm | | 640 nm | | 651 nm | | 672 nm | | |
| | 100% | 555.97 | 100.00 | 388.00 | 100.00 | 261.00 | 100.00 | 115.83 | 100.00 | 52.82 | 100.00 | |
| | PPE | | | | | | | | | | | |
| | 90–10 | 602.56 | 108.38 | 434.93 | 112.10 | 304.50 | 116.67 | 154.44 | 133.33 | 88.96 | 168.42 | |
| | 80–20 | 593.25 | 106.70 | 428.67 | 110.48 | 304.50 | 116.67 | 145.53 | 125.64 | 83.40 | 157.89 | |
| | 67–33 | 565.29 | 101.68 | 403.64 | 104.03 | 280.77 | 107.58 | 136.62 | 117.95 | 72.28 | 136.84 | |
| | 50–50 | 549.76 | 98.88 | 384.87 | 99.19 | 268.91 | 103.03 | 127.71 | 110.26 | 66.72 | 126.32 | |
| | 20–80 | 493.85 | 88.83 | 344.19 | 88.71 | 253.09 | 96.97 | 112.86 | 97.44 | 63.94 | 121.05 | |
| | 10–90 | 456.58 | 82.12 | 337.93 | 87.10 | 233.32 | 89.39 | 103.95 | 89.74 | 58.38 | 110.53 | |

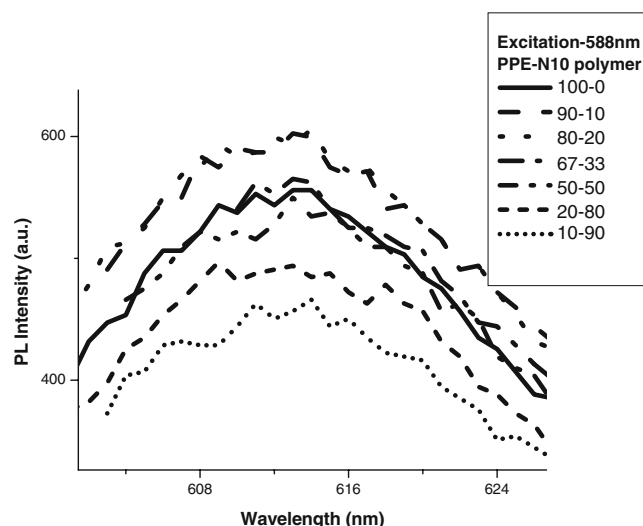


Fig. 2 Effect of N2 polymer composition on PPE emission intensity

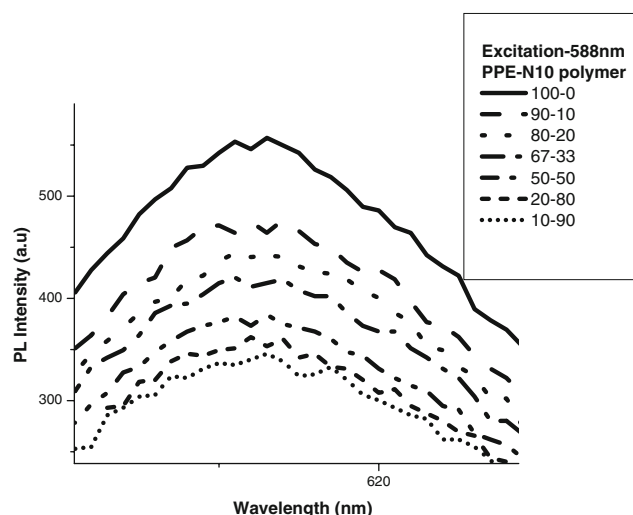


Fig. 3 Effect of N10 polymer composition on PPE emission intensity

651 nm emission only 5% variation in intensity is observed. In contrast to this, at an excitation of 588 nm, variation in the PL intensity value at 10% concentration increase with lower wavelengths of emission. i.e. for 613 nm emission, only 8% increase is seen in the intensity whereas for 672 nm emission, about 68% increase in the corresponding intensity is observed.

Unlike N2 polymer, which is having the spacer length of two carbon atoms, N10 polymer that contains lengthy alkoxy spacer of ten carbon atoms shows the characteristic variation in quenching of the photoluminescence of PPE (Table 5). Even though in both N2 and N10 polymer, the

intensity decrease with the increase of polymer concentration, in N10 with an initial addition of 10% of polymer to PPE quenches the value by 15% (excitation 588 and emission 613 nm as shown in Fig. 3). Whereas in N2 system, 10% addition of polymer enhance the intensity of emission by 40%. Comparison of HOMO, LUMO and HOMO-LUMO separations obtained from theoretical methods clearly indicate that N2 polymer has higher value than that of N10 polymer. Additionally of all the compound studied, N10 has the lowest LUMO value (−1.994 eV) [27]. This data can help us to understand the highest quenching obtained out of all the compounds studied.

Table 5 Effect of N10 polymer concentration on PPE emission intensity

| | PPE-N10 | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) |
|-----------------|---------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|
| N10 | | | | | | | | | |
| λ_{exc} | 545 nm | | | | | | | | |
| λ_{emi} | | 612 nm | | 621 nm | | 635 nm | | 647 nm | |
| | 100-0 | 184.24 | 100.00 | 143.02 | 100.00 | 87.98 | 100.00 | 50.00 | 100.00 |
| | 90-10 | 157.92 | 85.71 | 126.39 | 88.37 | 73.32 | 83.33 | 42.00 | 84.00 |
| | 80-20 | 152.28 | 82.65 | 116.41 | 81.40 | 64.16 | 72.92 | 40.00 | 80.00 |
| | 67-33 | 141.00 | 76.53 | 109.76 | 76.74 | 67.82 | 77.08 | 38.00 | 76.00 |
| | 50-50 | 127.84 | 69.39 | 98.12 | 68.60 | 60.49 | 68.75 | 34.00 | 68.00 |
| | 20-80 | 120.32 | 65.31 | 93.13 | 65.12 | 54.99 | 62.50 | 32.00 | 64.00 |
| | 10-90 | 112.80 | 61.22 | 88.14 | 61.63 | 53.16 | 60.42 | 30.00 | 60.00 |
| N10 | | | | | | | | | |
| λ_{exc} | 588 nm | | | | | | | | |
| λ_{emi} | | 613 nm | | 621 nm | | 635 nm | | 647 nm | |
| | 100-0 | 556.92 | 100.00 | 460.79 | 100.00 | 260.64 | 100.00 | 158.84 | 100.00 |
| | 90-10 | 464.10 | 83.33 | 410.78 | 89.15 | 231.68 | 88.89 | 144.21 | 90.79 |
| | 80-20 | 442.26 | 79.41 | 378.63 | 82.17 | 206.34 | 79.17 | 127.49 | 80.26 |
| | 67-33 | 414.96 | 74.51 | 360.77 | 78.29 | 202.72 | 77.78 | 123.31 | 77.63 |
| | 50-50 | 384.02 | 68.95 | 316.12 | 68.60 | 179.19 | 68.75 | 110.77 | 69.74 |
| | 20-80 | 353.08 | 63.40 | 305.41 | 66.28 | 168.33 | 64.58 | 102.41 | 64.47 |
| | 10-90 | 345.80 | 62.09 | 287.55 | 62.40 | 168.33 | 64.58 | 102.41 | 64.47 |

Table 6 Effect of R10 polymer concentration on PPE emission intensity

| | PPE-R10 | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) | Intensity | Factor (%) |
|-----------------|---------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|
| R10-series | | | | | | | | | |
| λ_{exc} | 545 nm | | | | | | | | |
| λ_{emi} | | 608 nm | | 613 nm | | 620 nm | | 636 nm | |
| | 100–0 | 174.72 | 100.00 | 184.91 | 100.00 | 162.00 | 100.00 | 87.84 | 100.00 |
| | 90–10 | 170.24 | 97.44 | 189.42 | 102.44 | 162.00 | 100.00 | 82.96 | 94.44 |
| | 80–20 | 197.12 | 112.82 | 207.46 | 112.20 | 180.00 | 111.11 | 97.60 | 111.11 |
| | 67–33 | 192.64 | 110.26 | 207.46 | 112.20 | 184.50 | 113.89 | 102.48 | 116.67 |
| | 50–50 | 192.64 | 110.26 | 207.46 | 112.20 | 184.50 | 113.89 | 102.48 | 116.67 |
| | 20–80 | 192.64 | 110.26 | 198.44 | 107.32 | 171.00 | 105.56 | 92.72 | 105.56 |
| R10-series | | | | | | | | | |
| λ_{exc} | 588 nm | | | | | | | | |
| λ_{emi} | | 613 nm | | 621 nm | | 637 nm | | 642 nm | |
| | 100–0 | 558.18 | 100.00 | 489.24 | 100.00 | 260.82 | 100.00 | 173.88 | 100.00 |
| | 90–10 | 558.18 | 100.00 | 493.77 | 100.93 | 251.16 | 96.30 | 165.60 | 95.24 |
| | 80–20 | 606.91 | 108.73 | 548.13 | 112.04 | 289.80 | 111.11 | 182.16 | 104.76 |
| | 67–33 | 633.49 | 113.49 | 543.60 | 111.11 | 313.95 | 120.37 | 186.30 | 107.14 |
| | 50–50 | 620.20 | 111.11 | 534.54 | 109.26 | 289.80 | 111.11 | 186.30 | 107.14 |
| | 20–80 | 593.62 | 106.35 | 520.95 | 106.48 | 275.31 | 105.56 | 190.44 | 109.52 |

The above concept can also explain the meager effect on quenching/enhancement of emission wavelength of PPE with R10 (Table 6). Comparison of N10 and R10 results clearly indicate that, even though the spacer length is same, N10 has the opposing polarization in the side chain. While the conjugation/polarization was extended in the side chain for R10. Because of this, R10 has lower HOMO-LUMO separation than that of N10. The results obtained with R10 are comparable to that of BTD and BIT since the HOMO, LUMO as well as band gap falls in the same range.

The above promising results in solution blends showed very high quenching with the slope value of -0.62 (for Excitation of 545 nm) -0.35 (for Excitation of 588 nm). This made us to study the influence of blend composition (PPE and N10) on photoluminescence in thin films. Thin films of chloroform solution were prepared by spin coating and the emission spectra of blend with varied concentration of polymer were computed. The results on the above studies indicate that at 50:50 N10–PPE blend showed the highest quenching of 85% in thin films (Fig. 4). Solution blend prepared for the same composition show quenching only around 30%. This can be visualized on the basis of the side chains present in PPE with rigid rod packing at room temperature.

Conclusions

Studies with different functionalized polythiophene with PPE are helpful to understand the influence of functional-

ized polythiophene structures on emission properties. In the case of N2 and N10 polymer even though the mesogenic side chain is the same except the spacer length indicate that the non-chromophoric spacer influence the emission quenching of PPE. Similarly comparison of R10 and N10 shows that the polarization and therefore the HOMO, LUMO and band gap of the polymer which ultimately controls the PL quenching of PPE. The results obtained by N10 thin films aids for the further studies to use them as photovoltaic materials.

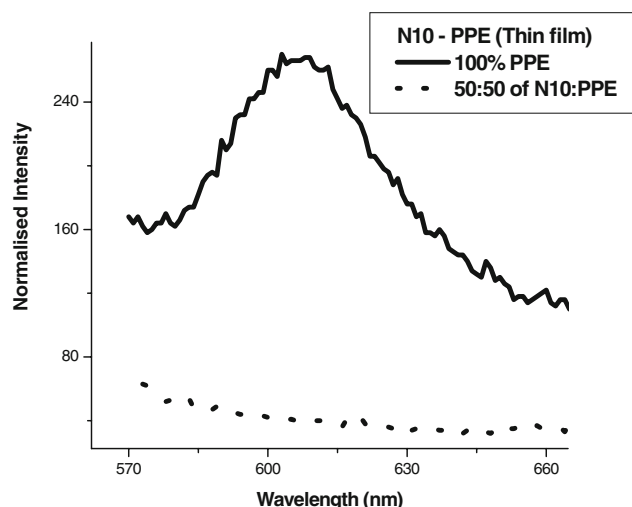


Fig. 4 Effect of N10 polymer composition on PPE emission intensity (solid state)

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