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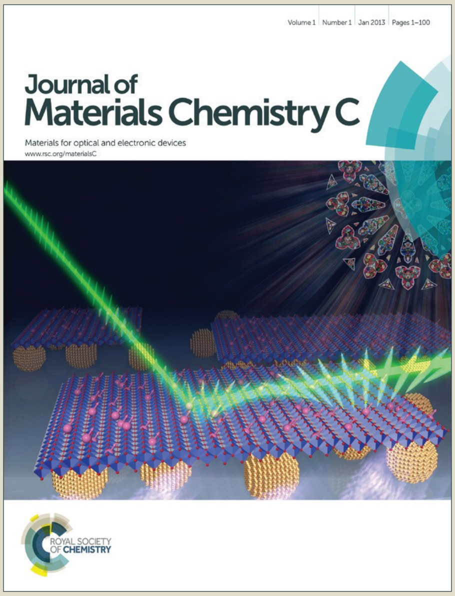

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Synthesis and Characterization of Color Tunable, Highly Electroluminescent Copolymers of Polyfluorene by Incorporating *N*-phenyl-1,8-Naphthalimide Moiety into Main Chain

Peddaboodi Gopikrishna,[a] Dipjyoti Das[a] and Parameswar Krishnan Iyer[a,b]

A series of six new organic light emitting copolymers were prepared from 9,9'-dioctylfluorene (DOF) and *N*-phenyl-1,8-naphthalimide (NPN) using palladium catalysed Suzuki polymerization. The feed ratios of Poly[2,7-(9,9'-dioctylfluorene)-*co*-*N*-phenyl-1,8-naphthalimide] (PFONPN) copolymers were 50:50, 65:35, 75:25, 90:10, 95:05 and 99:01 respectively. These copolymers have good thermal stability with onset decomposition temperature (T_d) of ~340-405°C and glass transition temperature (T_g) of 123-134°C. All the copolymers are highly fluorescentandsoluble in common organic solvents such as chlorobenzene, chloroform, dichloromethane, THF, toluene etc. allowing their processing from desired solvent. The electroluminescence (EL) properties of the copolymers were also studied by fabricating single layer devices with ITO/PEDOT: PSS/PFONPN/Ca: Al configuration. The PL and the EL spectra of the copolymers reveals that by changing the content of NPN moiety in the polyfluorene main chain from 1-50 mol %, the emission color of the polymers can be tuned from blue to green with Commission International de l'Echairage (CIE) coordinates being (0.17, 0.22) to (0.24, 0.49). This color tuning can be attributed to the strong energy transfer from the fluorene to NPN unit in the polymer backbone. The devices made with these copolymers are found to be very bright with PFONPN01 giving the highest brightness of 5236 cd/m^2 with a luminous efficiency of 3.52cd/A.

Introduction

Since the discovery of polymer light-emitting diodes (PLEDs) based on poly(p-phenylenevinylene) in 1990,[1] conjugated polymers (CPs) have attracted significant attention towards PLEDs due to their potential application in large-area, flat-panel displays because of their wide structural variety, low cost, very high flexibility and ease of processing.[2-5] In the past decades, polyfluorenes have been extensively used as active materials for multicolour PLEDs because of their excellent thermal and chemical stability, good solubility in common organic solvents, easy functionalization at the C-9 position of fluorene and high fluorescence quantum yields in solid films.[6] Generally polyfluorenes are p-type (electron donor) materials with large band gaps[7] and emit blue light. However, the emission color of polyfluorenes can be judiciously tuned over the entire visible region by introducing the narrow band gap units into the polyfluorene backbone as mentioned in few examples earlier.[8-20] The commonly used narrow band gap units are aromatic heterocyclic compounds such as benzothiadiazole,[8-10] bithiophene[15] and naphthoselenadiazole.[13] Recently organic molecules[21] and polymers[22-24] containing 1,8-Naphthalimide and its derivatives have generated lots of research interest as luminescent materials in organic EL devices due to their superior thermal, chemical and optical properties and high fluorescent quantum yields. Generally 1,8-Naphthalimide derivatives have high electron affinities (because they possess carbonyl groups) and demonstrate good electron transporting or hole blocking capabilities that can help balance the charge in PLEDs.[25] Introduction of electron donating substituents at 4-position of 1,8-Naphthalimide derivatives makes them highly fluorescent.[26-28] Unlike 1,8-naphthalimide containing side chains non-conjugated polymers which have the disadvantage of low light-emitting efficiency,[29-31] CPs containing 1,8-naphthalimide derivatives have emerged very promising as potential candidates for PLED applications owing to the possibility of energy transfer from the conjugated backbone to the low-band-gap 1,8-naphthalimide moieties.[22,32,33]Indeed, numerous organic light emitting homo polymers have been reported by incorporation of *N*-phenyl-1,8-naphthalimide derivatives into polyfluorene by end capping method.[34,35]Recently, few studies have reported that when *N*-aryl-1,8-naphthalimidederivatives were incorporated into the CP the resulting polymer could show large EL and PL efficiency.[33,35]

Herein, the synthesis, characterization and color tuning of a series of new donor and acceptor based, highly

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†Electronic Supplementary Information (ESI) available: ^{1}H and ^{13}C NMR scanned spectra of all the newly synthesized compounds and DSC curves are included. See DOI: 10.1039/x0xx00000x

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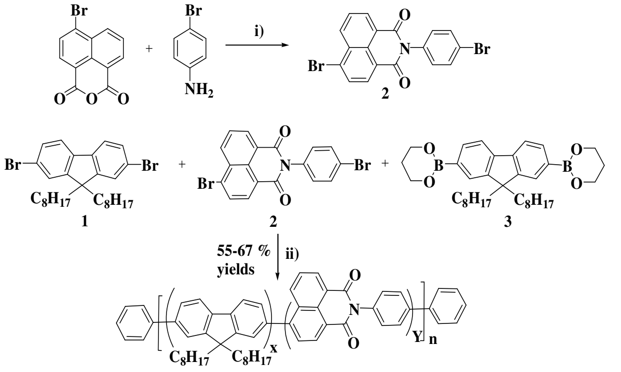
electroluminescent conjugated random copolymers derived from 9,9'-dioctylfluorene (DOF) and *N*-phenyl-1,8-naphthalimide (NPN) by Suzuki cross coupling reaction (scheme 1) is reported. The NPN co-monomer was inserted into polyfluorene main chain as an acceptor to enhance the electron transporting properties and to improve the recombination efficiency of holes and electrons. To the best of our knowledge, this is the first report of block copolymer using NPN unit with polyfluorene by Suzuki coupling reaction. By controlling the NPN unit in polymer main chain the emission color of polymer was tuned efficiently from blue to green. The emission color of copolymers changes when NPN content increases from 1-50 mol % into the polyfluorene main chain. We observed that in solid state PL, the polyfluorene fluorescence completely quenched even for 1 mol% of NPN content. We believe that the NPN unit allows efficient intramolecular energy transfer from the fluorene segment to the NPN unit. The EL spectra of these polymers show excellent color tuning and except PFONPN01, all copolymers showed only single peak because of strong energy transfer from the fluorene backbone to NPN unit. The emission spectra of the polymers were highly red shifted with gradual increment of NPN content in the polymer backbone. The devices made with these copolymers are found to be very bright with PFONPN01 giving the highest brightness of 5236 cd/m^2 with a luminous efficiency of 3.52cd/A.



Scheme 1. Synthetic route for monomer and polymers. Feed ratio of Monomers: 99/01 (PFONPN01), 95/05 (PFONPN05), 90/10 (PFONPN10), 75/25 (PFONPN25), 65/35 (PFONPN35), 50/50 (PFONPN50).i) Glacial acetic acid, Reflux, 12 hrs. ii)Pd(pph$_3$)$_4$, Aliquat 336, 2M K$_2$CO$_3$, THF, 48 hrs, Benzene boronic acid, Iodobenzene.

Results and discussion

Synthesis and characterization of the polymers

The synthetic routes to the preparation of monomers and polymers are shown in **scheme 1.** The monomers 2,7-dibromo-9,9'-dioctylfluorene (donor) **(1)** was prepared according to reported procedure[36] and 4-bromo-9-*N*-4-bromophenyl-1,8-naphthalimide (acceptor) **(2)** was prepared from 4-bromo-1,8-napthalicanhydride and 4-bromo aniline. Donor-Acceptor based random conjugated copolymers were synthesized from monomers 1, 2 and 3 using palladium (0) catalysed Suzuki coupling polymerization. The molar ratio of 4-bromo-9-*N*-4-bromophenyl-1,8-naphthalimide moiety in the copolymers was controlled by adjusting the molar ratio of 1 and 2 while maintaining a 1:1 molar ratio between the dibromo monomers and 9,9'-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol)ester. The colors of the PFONPN01, PFONPN05 and PFONPN10 polymer powders were light yellow and that of PFONPN35, PFONPN25 and PFONPN50 polymers were yellow.

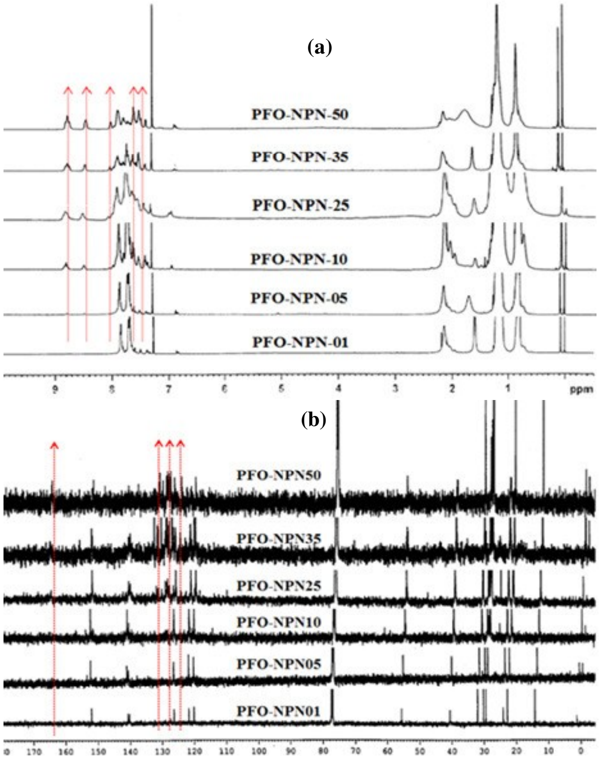


Fig. 1 ^{1}H (a) and ^{13}C NMR (b) spectra of polymers in CDCl$_3$.

The ^{1}H and ^{13}C NMR spectra (Fig. 1) of the polymers in chloroform-d, and FT-IR spectra (Fig. 2) confirmed the expected polymer structures. In ^{1}H NMR spectra we observed peaks at 8.75 and 8.44 ppm due to the NPN moiety protons along with some other peaks merged with fluorene peaks. Similarly, in ^{13}C NMR spectra, we observed peaks at 164.77, 132.53, 131.31, 130.31, 128.86, 128.20, 127.95 and 127.11 ppm due to the NPN moiety carbons. The relative intensity of NPN peaks in both the ^{1}H and ^{13}C NMR spectra gradually increases as the NPN moiety increases in the polymer chain.

Table 1 NPN content in the polymers.

NPN content in thePolymers (mol %)		
Polymer	Feed ratio	Actual content^a
PFONPN01	1	0.8
PFONPN05	5	5
PFONPN10	10	12
PFONPN25	25	28
PFONPN35	35	39
PFONPN50	50	48

^{a}Calculated from the ^{1}H NMR spectra.

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The actual content of NPN in the polymers was estimated from their ^{1}H NMR spectra by comparing the integral values of NPN unit with that of the fluorene monomer and are listed in Table 1. It is found that the actual content of NPN is very close to the feed ratio, suggesting that NPN has been fully incorporated into the main chain of the polymers during polymerization. In FT-IR spectra of the PFONPN polymers the five peaks located at 1710, 1669, 1585, 1357 and 1237 cm^{-1} correspond to the NPN unit, and with increasing NPN moiety in the polymer chain, the relative intensity of these five peaks also show an increase. All copolymers were soluble in common organic solvents such as chlorobenzene, toluene, chloroform, dichloromethane and THF.

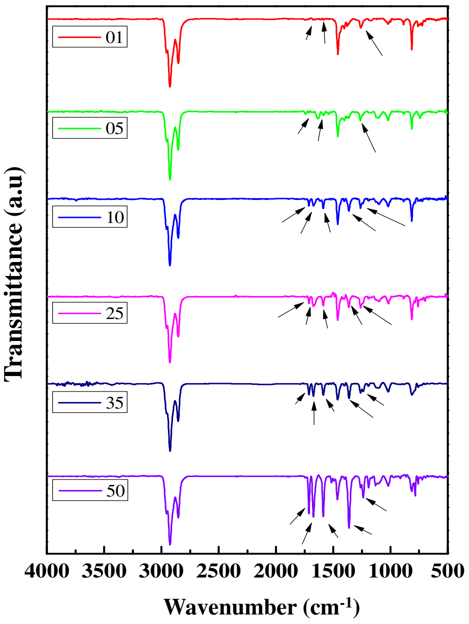

Fig. 2 FT-IR spectra of polymers.

Table 2 Polymerization results and Thermal data of polymers.

Polymer	M_n^{a}	M_w^{a}	PDI^a	Yield (%)	T_d^{b}(°C)	T_g^{c}(°C)
PFONPN01	12463	14622	1.31	58	388	134.20
PFONPN05	13389	15213	1.17	67	405	123.48
PFONPN10	12057	14032	1.16	55	344	132.23
PFONPN25	12135	14146	1.26	62	380	133.33
PFONPN35	11729	13663	1.14	57	355	125.46
PFONPN50	12568	14747	1.17	61	342	132.85

^{a}M_n, M_w and PDI of the polymers were determined by gel permeation chromatography using PMMA standards. ^{b}Onset decomposition temperature measured by TGA under nitrogen. ^{c}Glass transition temperature.

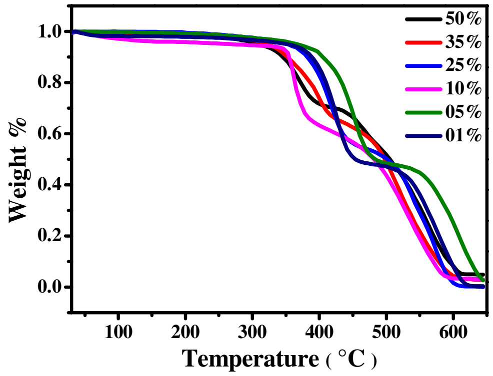

Fig. 3 TGA curves of polymers.

The number-average molecular weights (M_n) of the copolymers, determined by gel permeation chromatography using a PMMA standard in THF were found to be in the range of 11729–13389 with a polydispersity index (M_w/M_n) of 1.14 to 1.31 (Table 2).The polymerization results of the synthesized copolymers are summarized in Table 2.Thermal properties of these copolymers were determined by TGA and DSC (See ESI, figure S8) under nitrogen flow at a heating rate of 10 °C/min.The TGA curves of the copolymers are shown in Fig 3.All the copolymers were found to exhibit very good thermal stability with onset decomposition temperature (T_d) 342-405°C (Table 2) and no weight loss observed at lower temperature. Interestingly all copolymers showed two step degradation due to the presence of two different units in the polymer main chain. The glass transition temperature (T_g) of the copolymers were investigated by DSC (Table 2). The amorphous nature of all polymers was very useful in solution processing for PLED fabrication.

Optical and Photoluminescence properties

The normalized UV-visible absorption properties of the PFONPN conjugated polymers, both in solution (chloroform, 10^{-5} M) and solid state are shown in Fig.4 and the results are summarised in Table 3.In solution state PFONPN50 polymer shows two absorption peaks at 325 and 393 nm and remaining all polymers showed single peaks viz. PFONPN35 at 365nm, PFONPN25 at 370nm, PFONPN10 at 363nm and PFONPN05, PFONPN1 at 380nm.

For solid state measurements, the copolymer films with a thickness approximately of 80 nm was spin coated on glass substrate from a chloroform solution. In solid state also PFONPN50 showed two peaks at 327 and 395nm whereas the remaining polymers showed single peaks viz. PFONPN35 at 370nm, PFONPN25 at 375nm, PFONPN10 at 365nm, PFONPN05 at 381nm and PFONPN01 at 380nm. The optical band gaps (E_g) of all the polymers were estimated from the solid state of UV-visible absorption edges. Both solution and solid state absorption maximum of all copolymers showed slight blue shift with fraction of NPN content increased because increasing the fraction of NPN content in polymer main chain induces a decrease in the effective conjugation length of fluorene units.[37,38] The normalized PL spectra of the PFONPN conjugated polymers, both in solution (chloroform 10$^-$

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^{5} M) and solid state are shown in Fig.5 and the results are summarised in Table 3.

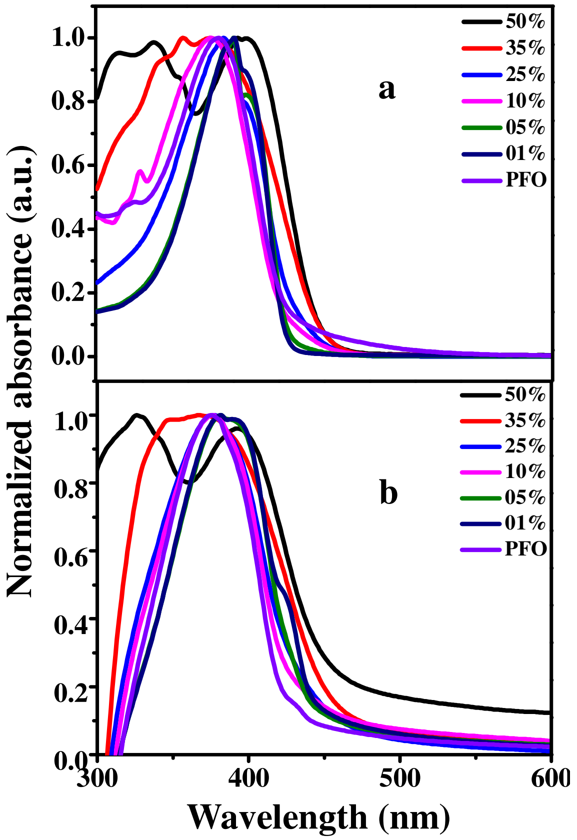

Fig. 4 UV-Vis absorption spectra of polymers in solution state (a) and solid state (b).

The solution state PL spectra of copolymers were taken at different excitation. The PL spectrum of PFONPN50 was taken under an excitation of 340nm, and single peaked at 508nmwas obtained. The emission color of the PFO is completely quenched due to energy transfer from the PFO to NPN unit.

All the remaining copolymers PFONPN35, PFONPN25, PFONPN10, PFONPN05 and PFONPN01 showed two peaks when excited at a wavelength of 380nm. The peak in blue region is due to fluorene unit whereas the peak in green region is because of the NPN unit. We observed that the intensity of the green peak increases on increasing the NPN unit in the polymer chain. All these copolymers showed single peak in solid phase due to efficient charge transfer and strong energy transfer from PFO to NPN units. The solid state PL spectra of the PFONPN50, was recorded at an excitation wavelength of 340nm whereas for the remaining copolymers the solid state PL spectra were recorded at an excitation wavelength of 380 nm. The emission colors of the polymers are red shifted from 466 nm to 511 nm (Blue to Green) when NPN content increases from 01 to 50 mol % in the polymer backbone.

The PL quantum yields (ΦPL) of the copolymers in solid state were measured with excitation at 380nm except PFONPN50 which was excited at 330nm (Table 3).The solid state quantum yields of the polymers are estimated by comparing their fluorescence intensity to that of a thin film sample of PFO polymer (ΦF = 0.55).[39] The quantum yield values of copolymers decrease with increasing numbers of the NPN unit due to the concentration quenching effect of the NPN unit due to aggregation of the chromophores.[22,40,41] A very good way to suppress this is by developing supramolecular compounds, such as rotaxanes, which suppress aggregation / quenching very effectively.[42]

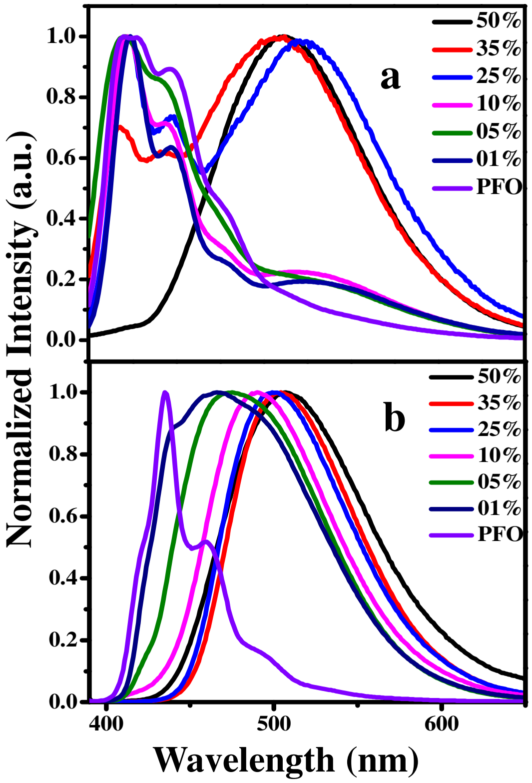

Fig. 5 Photoluminescence spectra of polymers in solution state (a) and solid state (b).

Table 3 Photo physical properties of the polymers.

	$CHCl_3$ solution		Solid state		
Polymer	$\lambda_{max,abs}$ [nm]	$\lambda_{max, PL}$ [nm]	$\lambda_{max, abs}$ [nm]	$\lambda_{max, PL}$ [nm]	Φ_{PL}^{c}
PFONPN01	380	415, 519	380	466	0.74
PFONPN05	380	415, 520	381	477	0.69
PFONPN10	363	415, 520	365	490	0.42
PFONPN25	370	416, 517	375	500	0.34
PFONPN35	365	416, 504	370	505	0.27
PFONPN50	325, 393	508	327, 395	511	0.18

[c] Solid state PL quantum yields are estimated with polydioctylfluorene standard.

Electrochemical properties

Cyclic voltammetry (CV) (Fig.6) was performed to investigate the reduction and oxidation peaks of the copolymers and to estimate their highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) energy levels.

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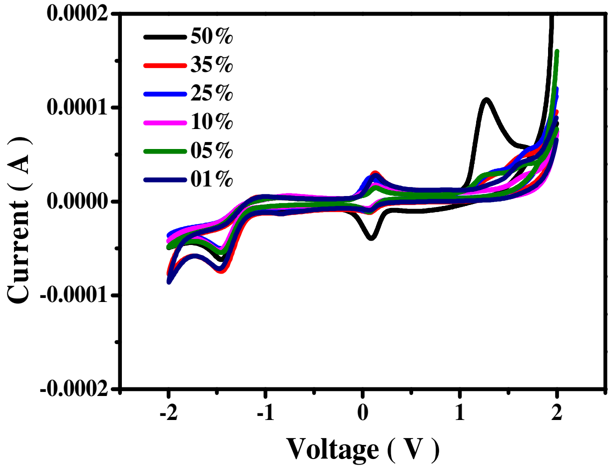

Fig.6 Cyclic Voltagramms of polymers.

The copolymers were drop casted onto carbon working electrode and silver and platinum wire were used as the reference electrode and counter electrode respectively. The electrochemical properties of the copolymers were investigated in an electrolyte consisting asolution of 0.1M tetra butyl ammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN) at room temperature under argon atmosphere.

Table 4 Electrochemical Potentials and Energy Levels of the PFONPN Polymers

Polymer	E_{ox}/V	E_{red}/V	E_{HOMO}/eV	E_{LUMO}/eV	E_g/eV	Optical band gap/eV
PFO	1.38	-0.69	-5.8	-2.9	2.9	2.95
PFONPN01	1.21	-1.2	-5.97	-3.5	2.47	2.71
PFONPN05	1.15	-1.3	-5.85	-3.4	2.45	2.70
PFONPN10	1.25	-1.16	-5.95	-3.52	2.41	2.69
PFONPN25	1.17	-1.2	-5.87	-3.5	2.37	2.67
PFONPN35	1.16	-1.18	-5.86	-3.5	2.34	2.62
PFONPN50	1.1	-1.23	-5.8	-3.47	2.33	2.52

The measurements were calibrated using ferrocene as standard. The PFONPN copolymers show two potential peaks (Fig. 6). The reduction potential, in negative potential region (-1.18 to -1.23V) is because of the NPN moiety as it has high electron affinity (because they possess carbonyl groups). Similarly, the peak in the positive potential region (1.1 to 1.25V) is oxidation potential and is for fluorene unit.The HOMO and LUMO energies were calculated by submitting the onset reduction and onset oxidation peak values in E_{LUMO} = [(E_{red} − $E_{1/2}$ (ferrocene)) + 4.8] eV, E_{HOMO} = [(E_{ox} − $E_{1/2}$ (ferrocene)) + 4.8] eV. The onset reduction and onset oxidation peak values, energy levels and band gaps of the copolymers were represented in Table 4.

Electroluminescence properties

In order to investigate the EL properties of the polymers, we fabricated single-layer devices with a configuration of ITO/ PEDOT:PSS(40 nm)/Polymer(80 nm)/Ca(10 nm)/Al(100 nm).

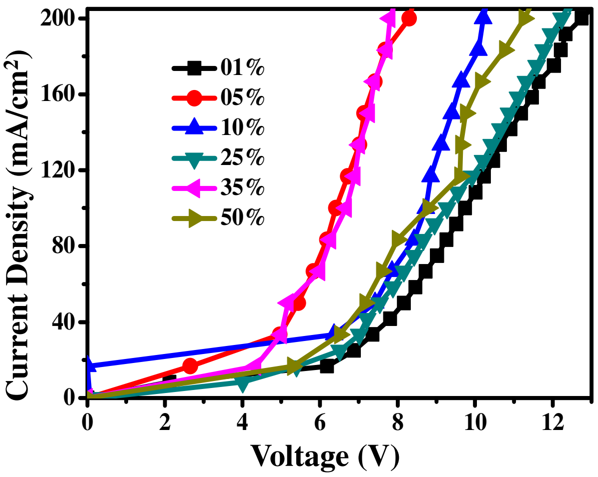

Fig. 7 Current Density-Voltage (J-V) characteristics of PLEDs.

The Current density-Voltage (J-V) characteristics and the typical EL spectra of all the PLEDs are shown in Figure 7 and 8 respectively. The onset values for all the fabricated devices along with their emission maxima and CIE coordinates are listed in Table 5. From Figure 8 it is clear that the copolymer PFONPN01 shows three peaks at 434 nm, 464 nm and 486 nm respectively. The first two peaks in the spectrum can be attributed to the polyfluorene main chain whereas the peak centred at 486 nm is due to the partial energy transfer from the PFO to NPN unit.[43-46] The polyfluorene emission, however, was completely quenched as the NPN content of the copolymer was increased.The EL spectra of all the other copolymers show only a single peak centred at 483 nm for PFONPN05, 493 nm for PFONPN10, 497 nm for PFONPN25, 504 nm for PFONPN35 and 506 nm for PFONPN50 respectively. The slight difference in wavelength between the solid state fluorescence emission and the electroluminescence emission can be attributed to the different emission mechanism between PL and EL.

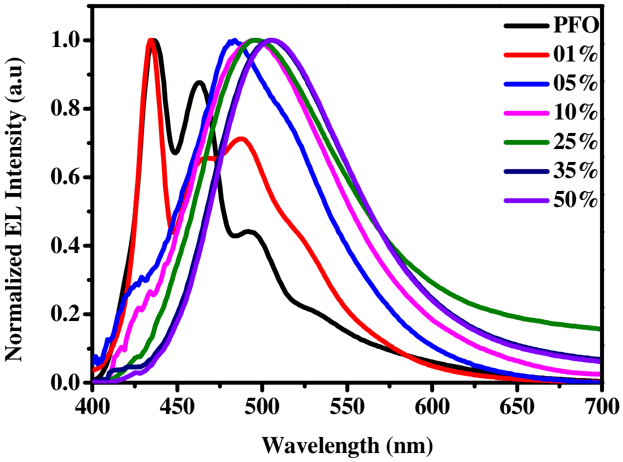

Fig. 8 Electroluminescence of PLEDs.

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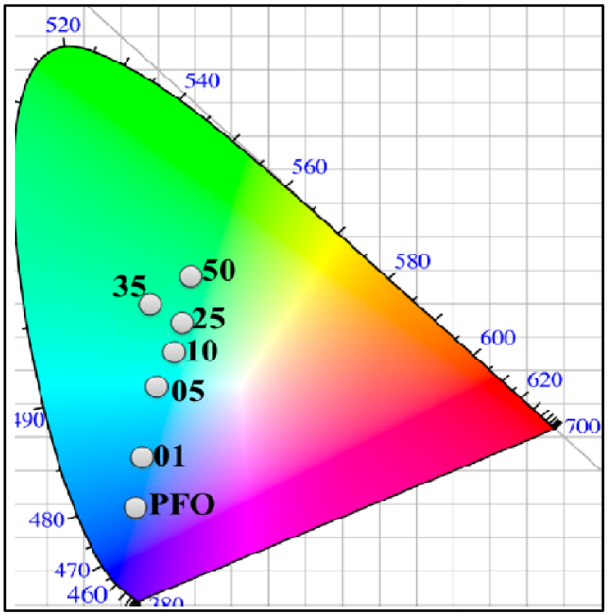

Fig. 9 Chromaticity diagram representing the CIE coordinates of the fabricated PLEDs.

Fig. 9 shows the chromaticity diagram representing the CIE coordinates of the fabricated PLEDs.The chromaticity coordinates of the copolymers changed from x=0.17, y=0.22, for PFONPN01 to x=0.24, y=0.49 for PFONPN50. The PLED devices fabricated using these copolymers are found to exhibit very good results and the device performance are presented in Table 5.Fig 10 and 11 shows that the brightness and current efficiency of the devices are 5236 cd/m^2 and 3.52 cd/A for PFONPN01, 3120 cd/m^2 and 1.96 cd/A for PFONPN05, 2064 cd/m^2 and 1.5 cd/A for PFONPN10, 1755 cd/m^2 and 1.16 cd/A for PFONPN25, 1756 cd/m^2 and 1.1 cd/A for PFONPN35 and 345 cd/m^2 and 0.22 cd/A for PFONPN50.The enhanced device performance of PFONPN01 as compared to other polymers results due to the well-balanced electron and holes in polymer main chain.From these results, it is clear that with increasing NPN content the device brightness showed a decreasing trend. This is due to the high electron affinity of NPN unit.

Table 5 Device Characteristics of PLEDs based on polymers.

Polymer	Onset voltage (V)	EL emission λ_{max} (nm)	Max. Brightness (cd/m^2)	Luminous efficiency (cd/A)	CIEcoordinate (*x*,*y*)^a
PFO	6.5	436, 463, 493	1949	0.99	0.17, 0.15
PFONPN01	6.3	434, 464, 486	5236	3.52	0.17, 0.22
PFONPN05	5.4	483	3120	1.96	0.19, 0.32
PFONPN10	6.5	493	2064	1.5	0.22, 0.45
PFONPN25	5.7	497	1755	1.16	0.22, 0.37
PFONPN35	5.3	504	1756	1.1	0.23, 0.42
PFONPN50	5.5	506	345	0.22	0.24, 0.49

^{a}Determined from the EL spectrum.

As the concentration of the NPN unit increases, the electron accepting capacity of the polymer also increases due to the excess of electron attracting effect leading to decreasing device performance.

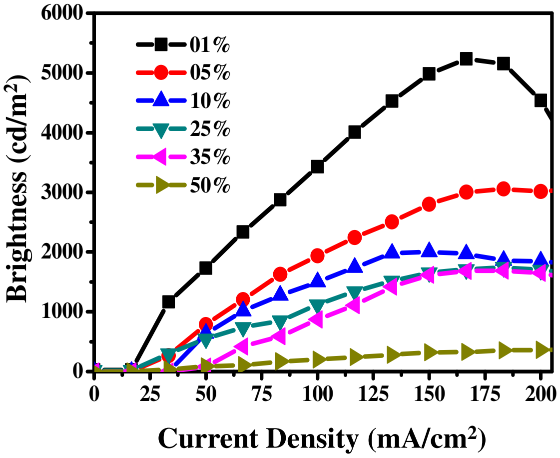

Fig. 10 Brightness Vs Current Density characteristics of PLEDs.

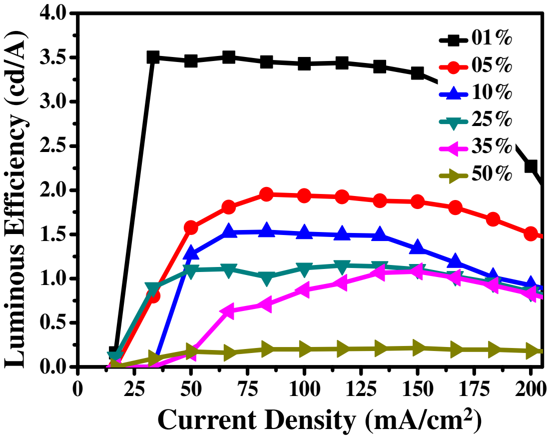

Fig. 11 Luminous Efficiency Vs Current density characteristics of PLEDs.

Conclusions

In summary, we have synthesized a novel class of donor and acceptor based random conjugated copolymers PFONPN by introducing NPN unit as an acceptor into the polyfluorene by well-known palladium catalysed Suzuki coupling reaction. All copolymers are highly soluble in common organic solvents such as chlorobenzene, chloroform, dichloromethane and THF. The resulting copolymers exhibit excellent thermal stability and high glass transition temperature. The emission color of the polyfluorene (blue) could easily be tuned to green via efficient energy transfer to acceptor (NPN) unit. In solid state photoluminescence, the polyfluorene fluorescence is totally quenched at NPN concentrations as low as 1% and the PFONPN copolymers exhibit maximum emission at 466-511nm. The single layer PLED devices made with these PFONPN polymers with configuration of ITO/PEDOT:

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PSS/PFONPN/Ca:Al are found to be very bright with PFONPN01 giving the highest brightness of 5236 cd/m^2 with a luminous efficiency of 3.52 cd/A. Like PL spectra, the EL spectra also show the color tuning property of the copolymers.

Experimental

Synthesis of 4-bromo-9-N-4-bromophenyl-1,8-naphthalimide (2)

4-bromo 1,8-naphthalicanhydride (0.500 g, 1.80 mmol), 4-bromo aniline(0.4649 g, 2.67 mmol) and 15mL glacial acetic acid were added into a 50mL round bottom flask at room temperature and refluxed for 12 hours. The reaction mixture was then cooled to room temperature and poured into distilled water (100 mL) the resultant solid was collected by filtration and recrystallized from acetone. (Yield 0.572 g, 73 %). ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.62-8.58(m, 2H), 8.36-8.34 (d, 1H) 8.27-8.25(d, 1H), 8.06-8.04 (t, 1H), 7.74-7.72(d, 1H), 7.39-7.37 (d, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm): 163.09, 163.03, 135.16, 133.68, 132.54, 131.71, 131.66, 131.42, 131.37, 131.07, 129.29, 129.16, 122.55, 121.51; Electrospray ionization mass spectrum (ESI-MS): $[M + H]^+$: calcd: 432.08; found: 432.2.

General polymerization procedure

9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, dibromo compounds (2,7-dibromo-9,9-dioctylfluorene and 4-bromo-9-*N*-4-bromophenyl-1,8-naphthalimide), 12 mL Tetrahydrofuran (THF) and tetrakis(triphenyl phosphine)palladium(0) (0.015 mmol) were added into a dry two neck round bottom flask. Subsequently 5 mL 2M aqueous potassium carbonate and aliquat 336 (0.025 mmol) were added to the flask. The reaction mixture was degassed thrice by freeze–thaw cycles to remove trace amounts of oxygen completely. The reaction mixture was stirred at 80 °C for 2 days, and iodobenzene was added as an end capper. After 4 hours, benzene boronic acid was dissolved in 1 mL THF and added into the reaction mixture as another end capper and stirring continued further for 4 hours. The reaction mixture was then cooled to room temperature, poured into 100 mL methanol and further stirred at room temperature for 4 hours. The desired polymer was collected by filtration and reprecipitated twice from methanol and acetone. The polymers were further purified by soxhlet filtration with acetone to remove oligomers and catalyst residues. After drying the polymers we obtained a yield of 55-67%. The resulted polymers were soluble in common organic solvents. The reactivity of the three different types of aryl-bromides differ under the reaction conditions reported herein. Fluorene unit has two identical bromides, whereas, the NPN unit has two different type of bromides, viz. attached to napthyl and phenyl rings. As compared to the NPN bromides the fluorene bromides are more reactive due to the absence of electron withdrawing group as well as its high electron density and there is a high possibility of oxidative addition predominatly. On the other hand, among the NPN bromides, the napthyl bromide is more reactive than the phenyl bromide since the napthyl moiety has more electron density. Hence, it has more feasibility to oxidative addition with palladium. In case of PFONPN01 to PFONPN35 we used three monomers viz. fluorene boronic ester, 2,7-dibromo-9,9'-dioctylfluorene and 4-bromo-9-N-4-bromophenyl-1,8-naphthalimide. In these copolymers, due to the high reactivity of fluorene bromide, there is a probability that it will react first with fluorene boronic ester forming a polyfluorene block. Similarly, the remaining fluorene boronic ester will react with 4-bromo-9-N-4-bromophenyl-1,8-naphthalimide forming another block. When they undergo polymerization, they may form copolymers containing long oligofluorenes segments. However, in case of PFONPN50, as we used only two monomers, viz. fluorene boronic ester and 4-bromo-9-N-4-bromophenyl-1,8-naphthalimide, it will form only alternating copolymers.

Poly[2,7-(9,9'-dioctylfluorene)-*co*-*N*-phenyl-1,8-naphthalimide (PFONPN50)

9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (3) (0.2792g, 0.50 mmol), 4-bromo-9-*N*-4-bromophenyl-1,8-naphthalimide (2) (0.2155g, 0.50 mmol), were used in this polymerization. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.75 (br, 2H), 8.42 (br,1H), 7.86 (br, 2H), 7.69 (br, 4H), 7.59 (br, 1H), 7.48 (br, 1H), 7.38 (br, 1H), 6.88 (br, 1H), 2.10 (br, 4H), 1.15 (br, 24H), 0.82 (br, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.64, 151.87, 140.71, 140.23, 131.60, 130.30, 129.30, 128.73, 128.27, 127.11, 124.98, 120.53, 55.88, 40.63, 31.99, 30.25, 29.44, 24.38, 22.82, 14.27; FT-IR (KBr pellets,cm^{-1}): 2953, 2922, 2850, 1710, 1669, 1585, 1466, 1357, 1237, 810.

Poly[2,7-(9,9'-dioctylfluorene)-*co*-*N*-phenyl-1,8-naphthalimide (PFONPN35)

9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (3) (0.2792g, 0.50 mmol), 2,7-dibromo-9,9-dioctylfluorene (1) (0.0822g, 0.15 mmol) and 4-bromo-9-*N*-4-bromophenyl-1,8-naphthalimide (2) (0.1508g, 0.35 mmol), were used in this polymerization. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.74 (br, 2H), 8.43 (br, 1H), 7.84 (br, 2H), 7.69 (br, 4H), 7.58 (br, 1H), 7.48 (br, 1H), 7.37 (br, 1H), 6.94 (br, 1H), 2.11 (br, 4H), 1.14 (br, 24H), 0.81 (br, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.77, 151.82, 151.70, 139.95, 132.53, 131.63, 131.31, 130.38, 128.86, 128.74, 128.68, 128.20, 127.95, 127.11, 126.85, 126.74, 126.11, 121.39, 120.27, 119.87; FT-IR (KBr pellets,cm^{-1}): 2953, 2922, 2850, 1710, 1669, 1585, 1466, 1357, 1237, 810.

Poly[2,7-(9,9'-dioctylfluorene)-*co*-*N*-phenyl-1,8-naphthalimide (PFONPN25)

9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (3) (0.2792g, 0.50 mmol), 2,7-dibromo-9,9-dioctylfluorene (1) (0.1371g, 0.25 mmol) and 4-bromo-9-*N*-4-bromophenyl-1,8-naphthalimide (2) (0.1077g, 0.25 mmol) were used in this polymerization. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.74 (br, 2H), 8.43 (br, 1H), 7.84 (br, 2H), 7.68 (br, 4H), 7.58 (br, 1H), 7.49 (br, 1H), 7.37 (br, 1H), 6.94 (br, 1H), 2.11 (br, 4H), 1.14 (br, 24H), 0.81 (br, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.57, 152.01, 140.71, 140.23, 132.33, 131.51, 130.67, 129.61, 129.19, 128.71, 128.46, 128.24, 127.13, 126.36, 121.70, 120.56, 120.15, 111.5, 55.54, 40.57,

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31.98, 30.22, 29.40, 24.12, 22.78, 14.24; FT-IR (KBr pellets, cm^{-1}): 2953, 2922, 2850, 1710, 1669, 1585, 1466, 1357, 1237, 810.

Poly[2,7-(9,9'-dioctylfluorene)-*co*-*N*-phenyl-1,8-naphthalimide (PFONPN10)

9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (3) (0.2792g, 0.50 mmol), 2,7-dibromo-9,9-dioctylfluorene (1) (0.2193g, 0.40 mmol) and 4-bromo-9-*N*-4-bromophenyl-1,8-naphthalimide (2) (0.0431g, 0.10 mmol) were used in this polymerization. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.79, (br, 2H), 8.44 (br, 1H), 7.87 (br, 2H), 7.70 (br, 4H), 7.57 (br, 1H), 7.49 (br, 1H), 7.37 (br, 1H), 6.88 (br, 1H), 2.12 (br, 4H), 1.14 (br, 24H), 0.82 (br, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 154.04, 140.73, 140.24, 126.38, 121.72, 120.18, 55.56, 40.60, 32.01, 30.25, 29.43, 24.14, 22.81, 14.26; FT-IR (KBr pellets,cm^{-1}): 2953, 2922, 2850, 1710, 1669, 1585, 1466, 1357, 1237, 810.

Poly[2,7-(9,9'-dioctylfluorene)-*co*-*N*-phenyl-1,8-naphthalimide (PFONPN05)

9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (3) (0.2792g, 0.50 mmol), 2,7-dibromo-9,9-dioctylfluorene (1) (0.2467g, 0.45 mmol) and 4-bromo-9-*N*-4-bromophenyl-1,8-naphthalimide (2) (0.0215g, 0.05 mmol) were used in this polymerization. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.75 (br, 2H), 8.44 (br, 1H), 7.85 (br, 2H), 7.70 (br, 4H), 7.56 (br, 1H), 7.49 (br, 1H), 7.37 (br, 1H), 6.83 (br, 1H), 2.1 (br, 4H), 1.14 (br, 24H), 0.80 (br, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 152.05, 140.74, 140.28, 126.39, 121.73, 120.19, 55.57, 40.59, 32.01, 30.26, 29.44, 24.14, 22.82, 14.28; FT-IR (KBr pellets, cm^{-1}) 2953, 2922, 2850, 1669, 1468, 814.

Poly[2,7-(9,9'-dioctylfluorene)-*co*-*N*-phenyl-1,8-naphthalimide (PFONPN01)

9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (3) (0.2792g, 0.50 mmol), 2,7-dibromo-9,9-dioctylfluorene (1) (0.2687g, 0.49 mmol) and 4-bromo-9-*N*-4-bromophenyl-1,8-naphthalimide (2) (0.0041g, 0.01 mmol) were used in this polymerization.^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.85 (br, 2H), 7.71 (br, 4H), 2.1 (br, 4H), 1.14 (br, 24H), 0.73 (br, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 152.04, 140.73, 140.24, 126.38, 121.72, 120.18, 55.56, 40.60, 32.01, 30.25, 29.43, 24.14, 22.81, 14.26; FT-IR (KBr pellets, cm^{-1}) 2953, 2922, 2850, 1468, 814.

Materials and Measurements

2,7-dibromofluorene, 1-bromooctane, 4-bromo 1,8-naphthalicanhydride, 9,9'-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol)ester (3), 4-bromoaniline, glacial acetic acid (99.85%), Tetrakis(triphenylphosphine)palladium(0), Aliquat 336, were purchased from Sigma-Aldrich and used without further purification. Chloroform, dichloromethane and toluene were distilled over calcium chloride and anhydrous tetrahydrofuran was dried over sodium-benzophenone. 2, 7-dibromo-9, 9'-dioctylfluorene (1) was prepared by following published procedures.[36]

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian AS 400 MHz and Bruker 600 MHz NMR spectrometers. UV-visible spectra were measured by PerkinElmer, Model Lambda-25 spectrometer. Photoluminescence spectra were recorded with Varian Cary Eclipse spectrometer. Electrochemical measurements were carried out under argon atmosphere on a deoxygenated solution of 0.1M tetra butyl ammonium perchlorate (TBAP) in acetonitrile by using CH instrument (Model 700D series). Glassy carbon as a working electrode, platinum as a counter electrode, and Ag/Ag$^+$ was used as reference electrode. Thermo Gravimetric Analysis (TGA) was recorded on Mettler Toledo, model TG/SDTA 851 e, Differential Scanning Calorimetry (DSC) was measured on a mettler Toledo, model DSC1, stare system. The gel permeation chromatography (GPC) measurements were recorded on waters 515 chromotograph connected to waters 2414 refractive index detectors by using tetrahydrofuran as an eluent and calibration curve of PMMA standards. FT-IR analysis was carried out with a Perkin-Elmer-Spectrum with samples prepared as KBr pellets.

PLED fabrication and characterization

In order to study the EL properties, PLEDs were fabricated using the as synthesized copolymers as active layer. The PLED device configuration is composed of a pre-cleaned and pre-patterned indium tin oxide (ITO) as the transparent anode. The ITO surface was ultrasonically agitated and cleaned in 2% detergent, acetone and isopropanol, each for five minutes at 60 °C. After cleaning, ~40 nm thin layer of poly (3,4-ethylendioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS) as a hole injecting layer was spin-coated at 3000rpm for 60 seconds, then baked for 15 minute in argon environment at 130 °C. The copolymers were dissolved in chlorobenzene (15 mg/mL) and spin-coated above the PEDOT:PSS layer under ambient atmosphere and thermally treated at 150 °C for 15 minute for the removal of residual solvent. The film thickness of the active layer was ~80 nm. Finally, calcium and aluminum was thermally evaporated at a rate of 0.1 Å/s and 10 Å/s respectively at a base pressure of 10-6 mbar to form the cathode electrode. The active area of the diodes was 12 mm^2. The current density-voltage (J-V) characteristics of the fabricated PLEDs were measured using Keithley 2400 source meter whereas the luminance and the EL spectra were measured using LCS-100 integrated sphere. All the devices were fabricated and characterized under Argon atmosphere inside a glove box.

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Table of contents entry

Synthesis and Characterization of Color Tunable, Highly Electroluminescent Copolymers of Polyfluorene by Incorporating N-phenyl-1,8-Naphthalimide Moiety into Main Chain

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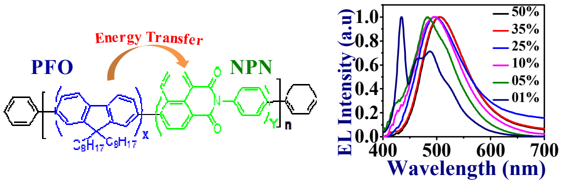

Block copolymers comprising N-phenyl-1,8-Naphthalimide (NPN) moiety into the main polyfluorene chain are introduced to tune the emission color in PLED devices. High performance devices are obtained by changing the NPN content in the polyfluorene main chain from 1-50 mol % thereby tuning the emission color of the PLEDs from blue to green with Commission International de l'Echairage (CIE) coordinates being (0.17, 0.22) to (0.24, 0.49).