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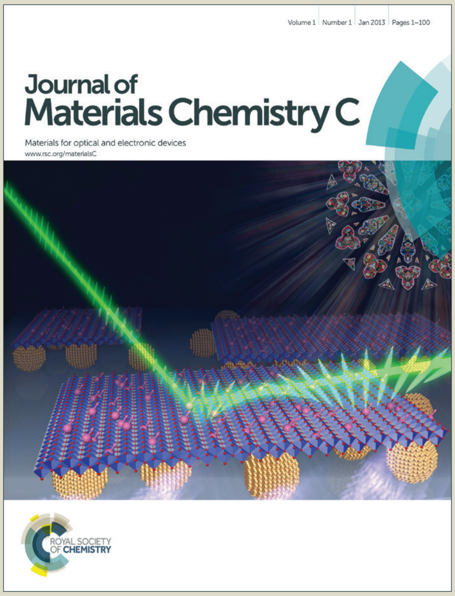

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PAPER

Offsetting the problem of charge trapping in white polymer light emitting diodes using a fluorenone based luminogen

Soundaram Jeevarathinam Ananthakrishnan,[a,b] Elumalai Varathan,[a,b,c] Narayanasastri Somanathan,*[a,b,c] Venkatesan Subramanian,[a,b,c] Asit Baran Mandal,[a] Janardanan D. Sudha[b,d] and Rajaraman Ramakrishnan[b,d]

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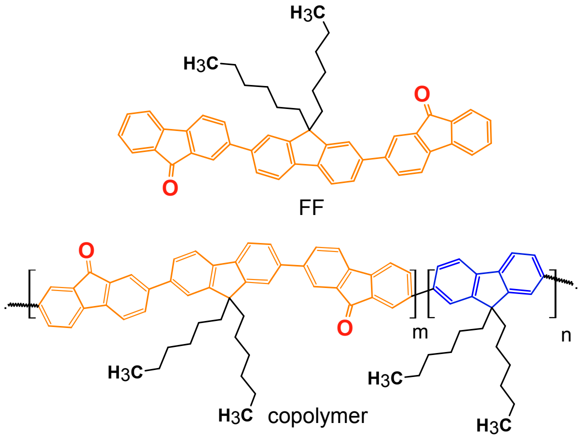
In this article we propose a strategy to offset charge trapping and enhance the confinement of excitons in the emissive layer of white electroluminescent copolymer using a luminogen with Aggregation Induced Emission Enhancement (AIEE). The fluorenone based luminogen, 2,7-bis(9H-fluoren-9-one-2yl)-9,9-dihelylfluorene (FF) that exhibited yellow emission with AIEE property is copolymerized with 9,9-Dihexylfluorene in different compositions to tune the color of emission. White light emission is demonstrated in a copolymer, FF-0.25 that contained 0.25% of FF in polymer back bone. Interestingly the copolymers exhibited enhanced emission upon aggregation in thin film even in low composition of FF. OLEDs fabricated from the copolymer FF-0.25 elicited a white electroluminescence with *Commission internationale de l'Eclairage* (CIE) coordinate of 0.30, 0.31 with power efficiency of 4.12 lm W^{-1}. FF-0.25 showed very low charge trapping compared to other white emitting single polymer OLEDs reported till date. The reduced charge carrier trapping is attributed to the positioning of energy levels in the copolymer that resulted in almost equal electron and hole injection barrier. A theoretical investigation on copolymers of FF revealed the presence of ambipolar property and low exciton binding energy implicit of efficient formation and confinement of excitons within the emissive layer. The system represents the first ambipolar white electroluminescent polymer designed by using a AIEE luminogen.

Introduction

White electroluminescent polymers presents a conceptually different way of light generation and signify a departure from conventional point source architecture to large area lighting and display applications.[1] These materials are steadily gaining interest of researchers owing to many advantages.[2] In general, the strategies used for development of White Organic Light Emitting Diodes (WOLEDs) included multilayer architectures with blend of various emitters, phosphoresent dopant in blue emitting polymers and multiple layers of phosphorescent emitters.[3-6] Apart from the above conventional techniques; some modest approaches like excited state intramolecular proton transfer[7] and supramolecular hydrogen bonding were also reported.[8] Nevertheless, the inherent problems like phase separation, alteration of recombination zone, field induced mobility change and complicated fabrication resulted in voltage dependent electroluminescence of multicomponent WOLEDs. [9-11]

Single white light emitting polymers are envisioned as smart and high fidelity systems for robust up-scaling by solution processing and with simple device architecture.[12, 13] White light emitting polymer were realized through different strategies for improved device performance.[14, 15] A survey of recent literature revealed that there has been a renewed effort by researchers to develop a high quality white electroluminescenct polymer with voltage independent output.[16] However, a majority of the white light emitting polymers reported till date exhibit a significant difference electroluminescence (EL) from photoluminescence (PL) due to charge trapping and consequent efficiency trade-off. The charge trapping in a single white light emitting polymer is manifested as superfluous long wavelength emission leading to significant difference between EL and PL. Charge trapping can be only partially avoided by using bipolar polyfluorene backbone as blue emitting units.[17]

Apart from the above developments Aggregation Induced Emission (AIE) presents a great potential to improve the efficiency of OLEDs by offsetting the Aggregation Caused Quenching (ACQ).[18, 19] Incorporation of AIE luminogens in conjugated polymers is very interesting since the AIE property can be transferred to the polymeric system.[20, 21] A polymer with AIE moiety was also demonstrated recently for application as down conversion layer for white light emitting diode and as emissive layer for monochromatic Polymer LEDs.[22] Supramolecular π-gel forming pyridinium salt based AIE luminogens were demonstrated to show white emission albeit



m = 0.5, n = 0.5 FF-50; m = 0.25, n = 0.75: FF-25
m = 0.10, n = 0.90: FF-10; m = 0.05, n = 0.95: FF-5
m = 0.01, n = 0.99: FF-1 ; m = 0.0025, n = 0.09975: FF-0.25

Chart 1. Structure of FF oligomer and its Copolymers.

with temperature dependence in solution state.[23]

Most of the afore mentioned systems were designed upon the principle of restricted intramolecular rotation (RIR) and reduced π-stacking interaction in solid state.[24] However, we have recently reported a novel luminogen, 2,7-bis(9H-fluoren-9-one-2yl)-9,9-dihelylfluorene (FF) with Aggregation Induced Emission Enahncement (AIEE) using fluorenone moieties by employing low transition dipole moment as a principle tool.[25] The luminogen, FF exhibited a bright yellow emission with quantum yield of 79%. However, white light emission from single conjugated polymers with AIE luminogenic moieties is not reported yet.

In this work we report on the synthesis, luminescence properties and OLED application of the copolymers synthesized using AIEE luminogen, FF (Chart 1).

A stable white light emission is demonstrated in a single polymer OLEDs with device configuration of ITO/PEDOTE:PSS/Polymer/Al based on a copolymer, FF-0.25. FF-0.25 showed no surplus long wavelength emission between EL and PL due to significant reduction of charge trapping. The above property is attributed to unique positioning of energy levels of FF. Apart from the above advantage, FF-0.25 was found to possess almost equal electron and hole injection barriers. Theoretical investigation of the copolymeric system revealed that the incorporation of FF in copolymer resulted in almost equal electron and hole reorganizational energies with rediuced exciton binding energy. To the best of our knowledge FF-0.25 represents the first white light emitting copolymer with AIEE luminogenic units.

Results and Discussions

Some of the notable works on fluorenone containing polymers and oligomers were studied as model system of keto defects (fluorenone defects) in polyfluorene.[26, 27] These defects were found to be source of green emission that was detrimental to purity of blue light emitted by polyfluorenes.[28] A significant amount of work has been done for elimination of keto defects by removing mono alkylated moieties.[29] Green emission from fluorenone defect was envisaged as a promising source for stable green LEDs.[30] Fluorenone defect was also utilized to develop white lighting polymers albeit by blending of a red emitter.[31, 32] In contrast to the above studies, a systematic investigation of copolymers of 9,9- Dihexylfluorene and fluoreneone trimer, FF with AIEE property is presented in the following sections.

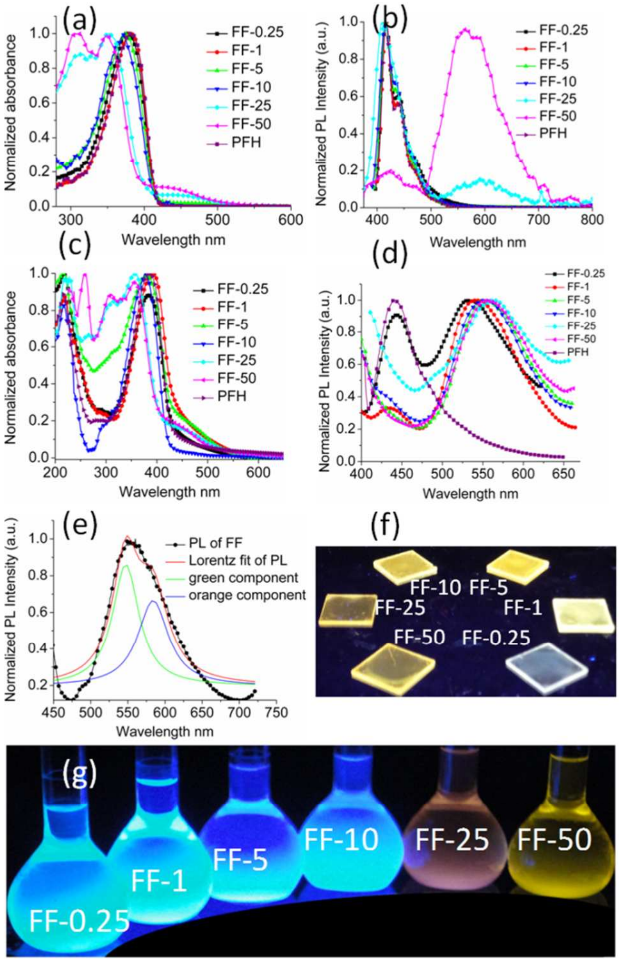


Figure 1. (a) Absorption, (b) PL spectra in THF solution; (c) Absorption, (d) PL spectra in spun thin films of copolymers. (e) Lorentzian fit for PL spectra of FF thin film; (f) spun thin films, (g) THF Solutions of copolymers under irradiation at ~360nm.

Spectral properties of monomer and copolymers

The absorption and emission spectra of the polymers are presented in Figure 1(a-d). The polymers showed a sharp change in wavelength of absorption with the change in composition of FF moieties in the main chain. FF-25 and FF-50 exhibited two absorption peaks at around 350 and 310 nm along with a low energy shoulder at ~430 nm that are very close to that of pure FF due to high content of FF units. Low energy absorption shoulder observed in FF-25 and FF-50 can be attributed to charge transfer transition from fluorene to fluorenone units.[33] The copolymers, FF-10 to FF-0.25 with low composition of FF units exhibited almost similar absorption spectrum with strong absorption peak at ~ 375 nm which is attributed to π-π* transitions. Further the long wavelength absorption shoulder at ~430 nm was observed as a weak band for FF-10 while the same in other polymers was not observed owing to low composition of FF units in polymer.

In thin films, FF-25 and FF-50 showed π-π* transitions as two prominent peaks at 311 and 356 nm that are very close to their solution absorbance values. The long wavelength CT band was observed at 451 and 458 nm for FF-25 and FF-50 respectively.

The emission spectra of the polymer in solution and thin film state revealed some important information on the mode of energy transfer within the polymer. In solution state the polymers with low composition of FF units (FF-0.25 – FF-10) showed complete blue emission which is in total contrast with previous observation on model systems with fluorenone defects that showed predominant emission at 535 nm.[34] FF-25 and FF-50 exhibited a weak emission at ~ 585nm and ~ 570 nm in solution state indicating a energy transfer to FF units. The long wavelength emissions of FF-25 and FF-50 also differed from that of polyfluorenes with fluorenone defects.[34]

The difference in emission of copolymers FF-0.25 to FF-10 between solution and solid film state can be understood as follows. In solution state even though there is a partial energy transfer from dihexylfluorene moieties to FF units, the AIEE property of FF units render them less emissive in solution state. In thin film state the emission of FF is turned on and hence the partial transfer of energy from dihexylfluorene to FF units lead to predominantly long wavelength emission. The low quantum yield of FF-25 and FF-50 (20.2 and 20.1respectively, Table S2†) in solutions can be attributed to energy transfer to FF units that are less emissive in solution state. Another factor which possibly may affect the process of energy transfer is the relative rate at which energy transfer and emission from dihexylfluorene moieties take place. Since energy transfer is a distance dependent process, in solution the average distance between the donor groups (dihexylfluorene) to acceptor (FF units) is high compared to that thin film state. Hence in thin film state energy transfer becomes significant and the high emission of FF moieties in thin film state lead to long wavelength emission. In FF-0.25, however the very low composition of FF units controls the intensity of long wavelength emission in thin film state. Thus FF-1 and FF-0.25 elicited dual emission at ~440nm and ~550nm with enhanced quantum yield of 64.0% and 72.8% respectively (Table S2†). As a result, white emission was observed for FF-0.25 and a yellow tinged white light was observed for FF-1.

Realization of white light emission with high purity from FF-0.25 can be understood from a lorentzian fit on the PL spectrum of FF in thin film. Thus the PL spectrum of FF thin film showed two peaks at 550nm and 586 nm that correspond to green and orange emissions respectively (Figure 1(e)) thus explaining the yellow emission from FF thin films by additive colour mixing.[35] Hence, copolymerization of FF units in appropriate proportions with blue emitting polyfluorene resulted in high purity white light emission in thin film by primary colour mixing albeit with just two component.[36]

Aggregation and decay of excited states

Aggregation properties of AIE luminogens have been extensively studied by using Dynamic Light Scattering (DLS) and Fluorescence Lifetime analysis (FLT).[37] DLS and FLT of aggregates, were studied simultaneously under identical conditions as used for fluorescence and absorption studies of polymers.[38]

The fluorescence lifetime of copolymers were measured in both solution and thin film state to understand the effect of aggregation on decay dynamics of excited states. The short and long lived decay channels of the copolymers can be correlated to the amount of non-aggregated and aggregated states.[39] The decay dynamics can be divided in to two different regime namely; under high and low compositions of FF units in copolymers.

Table 1. Fluorescence Lifetime (FLT) and Dynamic Light Scattering (DLS) data of copolymers.

Polymer	Fluorescence life time		DLS
	Solution	Thin film	
	[a]τ_1/τ_2 (a_1/a_2)	[b]$T_1/T_2/T_3$ ($A_1/A_2/A_3$)	[c]R_H (I)
PFH	6.35/0.57 (1.2/98.8)	4.16/0.29 (12.1/87.9)	271.5/35.09 (47.4/53.6)
FF-0.25	2.55/0.57 (13.6/86.4)	6.21/2.04 (56.4/43.6)	349/38.68/5.14 (38.6/41.1/20.3)
FF-1	5.90/0.59 (1.1/98.9)	5.73/2.04 (68.0/32.0)	495.8/119.6/13.25 (36.5/39.6/23.9)
FF-5	6.22/0.64 (1.0/99.0)	3.86/1.31 (64.0/36.0)	141.7/20.9/7.8 (35.8/33.2/31.0)
FF-10	5.61/0.66 (1.2/98.8)	5.02/1.67 (74.5/25.5)	350.2/211.10/9.70 (40.1/44.0/15.9)
FF-25	5.80/3.01 (74.1/25.9)	5.19/2.17 (72.5/27.5)	223.3/51.42/7.59 (64.2/14.6/19.2)
FF-50	6.62/3.55 (46.6/53.4)	4.86/1.32 (10.9/89.1)	716.8/9.72 (52.0/48.0)

[a] τ_1/τ_2, Life time of different decay channels from FLT experiment in ns; a_1/a_2, % contribution of different decay channels in THF solution. [b] $T_1/T_2/T_3$, Life time of different decay channels from FLT experiment in ns; $A_1/A_2/A_3$, % contribution of different decay channels in thin films. [c] R_H, Hydrodynamic radii in nm; I, % composition of different species with corresponding R_H values.

In case of FF-0.25, FF-1, FF-5 and FF-10 with low composition of FF units, a predominant ultrafast decay channel was observed with life time <1ns similar to poly(9,9-dihexylfluorene)-2,7-diyl (PFH) used as a control for this study (Table 1). However, the ultrafast decay channel was not observed for the same copolymers in thin film state where slow decay channels became predominant (Table 1).[40]

For copolymers with high content of FF units, the ultrafast decay channel was not observed in both solution and thin film states. The relative contributions of different decay channels were equal in solution and thin film states of FF-25. FF-50 showed a overall decrease in the life time of decay channels in thin film state relative to that in solution. The reduced life time of decay channels in FF-50 is similar to the behavior of pure FF due to aggregation induced planarization.

DLS data of fluorescent organic molecules can be correlated to study their aggregation.[41] DLS data of these polymers suggested there is a extensive aggregation in all polymers in solution state as evident from the trimodal distribution of hydrodynamic radii (R_H). Further, trimodal distribution observed for copolymers of FF indicate a sharp contrast to PFH. Thus FF units even if present in low proportions in copolymers strongly influenced the optical properties by aggregation effect of fluorenone moieties in solution and thin film state.

Aggregation Induce Emission Enhancement

The copolymers with high composition can be considered as more polar due to fluorenone content while the copolymers with

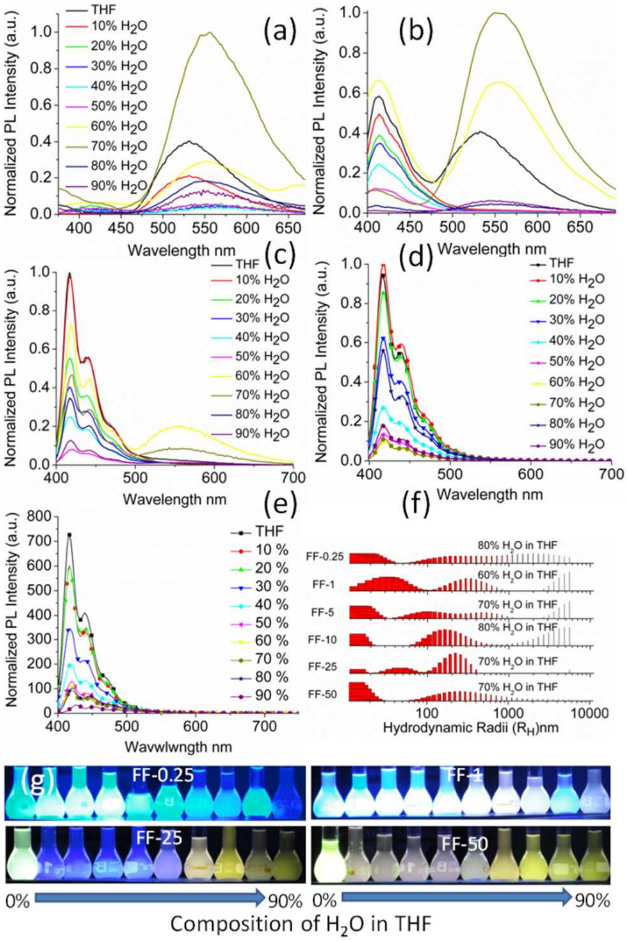


Figure 2. PL spectra of (a) FF-50, (b) FF-25, (c) FF-1, (d) FF-0.25, (e) poly 9,9-Dihexylfluorene-2,7-diyl (FHP) in THF-water mixtures; (f) DLS traces of copolymers and (g) photograph of copolymer upon irradiation with ~360 nm in different THF-water mixtures.

lower composition of FF units are hydrophobic owing to high content of 9,9-dihexylfluorene units. In addition to the above fact, the FF units present in the copolymer can be viewed to contribute to Aggregation Induced Emission Enhancement (AIEE) property while 9,9-dihexylfluorene will impart a Aggregation Caused Quenching (ACQ) effect. The properties of the copolymers can be viewed as interplay of these properties. The copolymers, FF-50 and FF-25 showed a weak emission in pure THF solution that was initially quenched in low compositions of water in THF due to the increase in polarity of the medium that leads to stabilization of charge transfer state by micro-environment.[42] However, intensity of emission increased when the composition was 60% of in THF and maximum intensity was observed at 70% water in THF due to the AIEE property of FF. Both FF-50 and FF-25 showed lower emission in mixtures containing 80 and 90% water in THF owing to extensive precipitation that lead to formation of bigger particles leading to scattering (Figure 2).[43] The precipitation of polymers in higher composition of water is also evident from the broadened absorption peaks (Figure S3†). In both FF-50 and FF-25, the bathochromic shift in emission relative to that in respective pure THF solutions indicating the formation of J-aggregates that induces higher fluorescence efficiency.[44]

In case of FF-10 a maximum emission was observed at 40% water in THF (Figure S4†) and further increase in water content resulted in quenching of emission due to precipitation that lead to effective reduction of concentration of polymer. FF-1 showed an interesting observation wherein a new low energy peak at ~556 nm (typical of FF units) was observed with partial enhancement in emission at 60% water content. The emergence of low energy emission in case of FF-1 copolymer upon aggregation can be attributed to the AIEE property of FF units. However, in the case of FF-1 the low intensity of emission at ~560 nm is controlled by the low composition of FF units. Thus, emergence of low energy emission peak in FF-1 aggregates resulted in a white light emission as presented in Figure 2(c) signifying a dual-channel fluorescence response (DCFR).

FF-0.25 showed an enhanced emission with maximum intensity at 10% water in THF and a partial increase in emission at 80% water-THF mixture. The maximum intensity at 10% water content can be attributed to hydrophobic nature of 9,9-dihexylfluorene moieties that resulted in the precipitation of FF-0.25 copolymer at low composition of water. The blue emission observed in aggregates of FF-0.25 is in contrast to white emission observed in thin film. The difference in emission property of FF-0.25 copolymer can be attributed to the low composition of FF units that are less emissive in polar medium that resulted from addition of 10% water in THF.[42] At high composition of water, the process of precipitation resulted in quenching of emission.

The precipitation is also evident from the broad absorption spectra of polymers (Figure S3†) and size of aggregates in micrometer range observed in DLS measurements of dispersions with partial enhancement in emission in case of FF-10, FF-5, FF-1 and FF-0.25 copolymers (Figure 2 c, d; Figure S4†). On the other hand, the initial quenching of emission in all copolymers is attributed to increased polarity and solvation effect in THF-water mixture on polar fluoreneone units.[45]

The above observations clearly indicate that the AIEE property of FF was very influential even when present in very compositions as low as 0.25%. The minimum composition of FF units of 0.25% is lesser than the 10% minimum composition of tetraphenylethylene (TPE) moieties in polyfluorenes required to actuate AIE property.[46, 47] The results were verified by a control experiment where PL spectra of poly 9,9-dihexylfluorene (PFH) was studied in different THF-water mixtures. The control experiment with PFH showed a complete quenching which is in total contrast to that of copolymers.

Ordering and Morphology of copolymers

The GIXRD traces and AFM of the copolymers are presented in Figure 3. The AFM micrograph of FF-0.25 showed lamellar structures which is different poly(9,9-Dihexylfluorene) (PFH) is interesting since the FF units are present in very low compositions.[48, 49] The change in morphology of FF-0.25 can be correlated with scattering at 6.1° 2θ corresponding to 14.4 Ǻ which is higher than that observed for β-phase of PFH which was typically observed at 10.8 Ǻ.[50] The reflection at ~ 6.1˚ 2θ was also observed for FF-1 that indicate a characteristic metastable β-phase responsible for enhanced quantum yield and thus justifying the high quantum yield for all copolymers in thin film state.[51]

For FF-5 copolymer, the reflection corresponding to β-phase was observed at ~5.1˚ 2θ that corresponded to d-spacing of 17.31

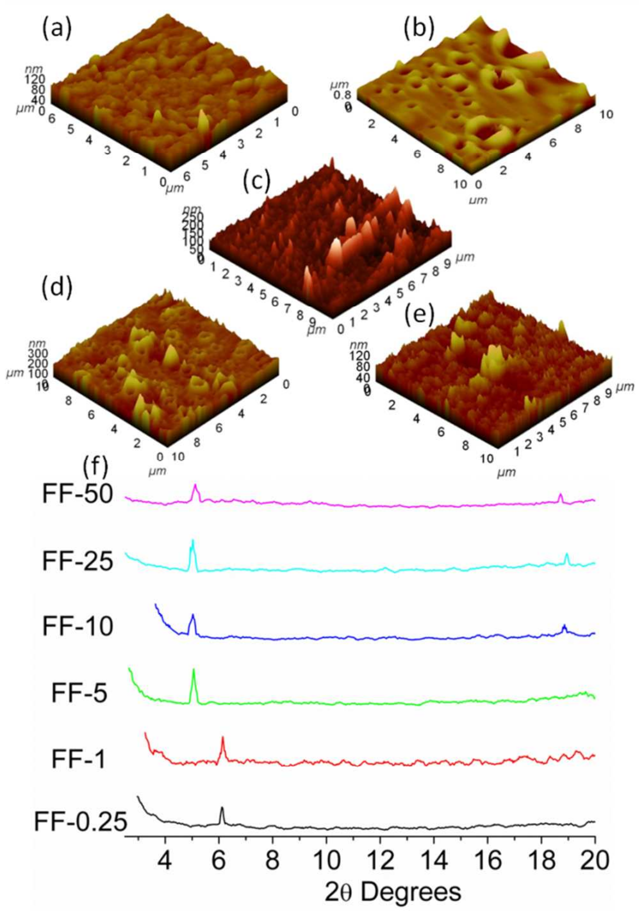


Figure 3. AFM micrograph of (a) FF-0.25, (b) FF-1, (c) PFH-FF, (d) FF-5, (e) FF-10 and (f) GIXRD traces of copolymers.

Ǻ. The reflection at ~5.1˚ 2θ was also observed for other copolymers with higher composition of FF units. The change in d- spacing of β-phase can be attributed to the increase of FF moieties in the main chain (Figure 3(f)).

Higher composition of FF units beyond 5% resulted in the emergence of a new reflection at ~18.9˚ 2θ (4.7 Ǻ) corresponding to the presence of cofacial stacking interactions of fluorenone units. Nevertheless, the d spacing of 4.7 Ǻ observed for FF-10, FF-25 and FF-50 is higher than the π-stacking interaction for eximer formation observed to be 3.5 Ǻ for fluorenone based model systems.[52] Thus, the copolymers with fluorenone cofacial interaction distance higher than that required for eximer formation between fluorenone moieties elicited higher quantum yield.[52] The absence of reflections centered at 18.9˚ 2θ in the case of FF-0.25, FF-1 and FF-5 can be attributed to very low composition of fluorenone containing FF units in polymer backbone.

In the case of FF-1 radial supramolecular assemblies appeared which was more prominently observed for FF-5 copolymer. The prominence of radial assemblies can be correlated to the shift in β-phase reflection in GIXRD traces of FF-5 (Figure 3(f)). The radial structures progressively vanished on further increase of FF composition in case of FF10, FF-25 and FF-50. The vanishing of radial assemblies can be further be correlated with prominent fluorenone cofacial interactions as evident from GIXRD peak at ~18.9˚ 2θ.

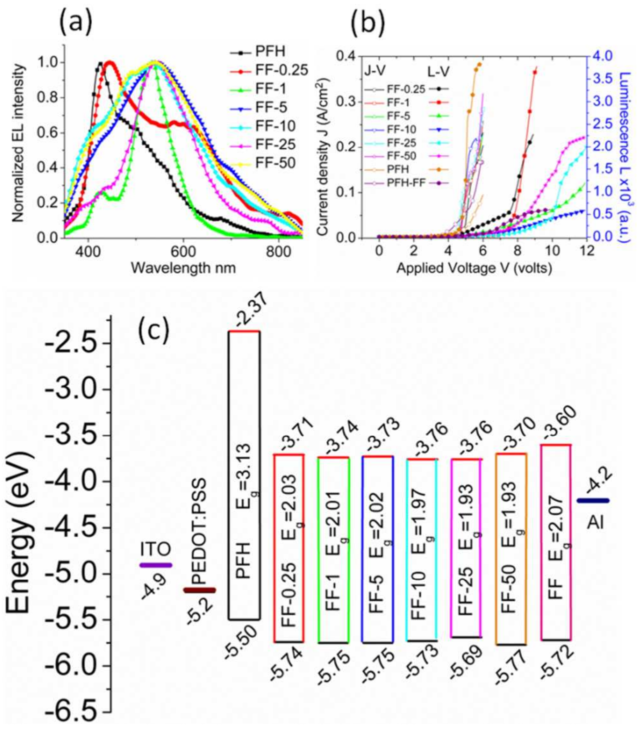


Figure 4. (a) EL spectra of copolymers and PFH (b) Current density-voltage (J-V) and Luminescence - voltage (L-V) plots of OLEDs, (c) Energy level diagram of polymers.

It is to be noted that the characteristic broad *amorphous halo* centered at ~21˚ 2θ and with an onset at ~10˚ 2θ in the case of pure poly(9,9-dihexylfluorene)-2,7-diyl (PFO) was not observed for all copolymers indicating very low proportions of disorder in films of copolymers. The copolymers exhibit a complete contrast in molecular and micro level ordering from PFH.

A blend of 0.25% of FF with PFH (PFH-FF) was prepared and studied for its morphology since it can reveal some details of energy transfer.[53] The morphological features did not exhibit any supramolecular assemblies and the average roughness of the film was found to be higher compared to the single copolymer with same composition of FF units (FF-0.25). Presence of some sharp variations of height in film of PFH-FF signifies some amount of inhomogenity.[53] The height of morphological features of copolymers FF-50 and FF-25 with high content of FF units were also found to be lesser than PFH-FF blend (Figure S4†). In case of copolymers, FF-1 and FF-5 height of morphological features were found to be higher than PFH-FF.

Device characteristics and decreased career trapping

Polymer Light Emitting Diodes (PLEDs) were fabricated from the copolymers with device configuration of ITO/PEDOT:PSS/ polymer/Al. The device characteristics of copolymers were studied for their electroluminescence at different voltage and interestingly the copolymers exhibited bright electroluminescence and low turn on voltage (Figure 4(b)). A close view of electroluminescence spectra of copolymers showed a yellow emission for FF-50 with a CIE coordinate of (0.38, 0.45) which is same as that of PL (Figure 5 and Table S3†). FF-50 displayed a maximum power efficiency of 5.77 lm W^{-1} while

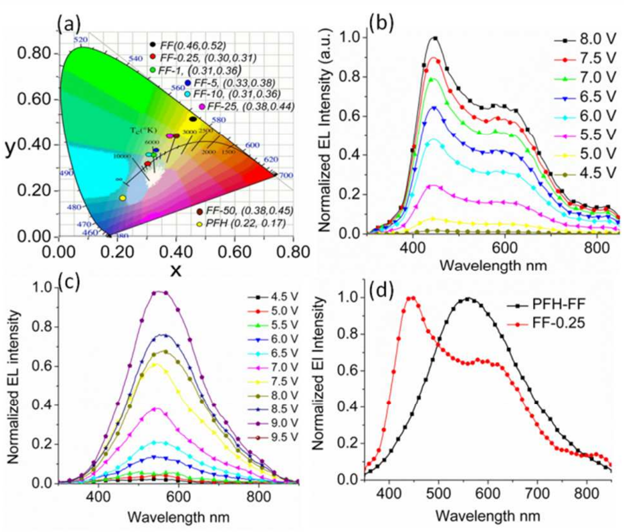


Figure 5. (a) CIE coordinates of polymers; EL spectra of (b) FF-0.25, (c) PFH-FF at different applied voltage and (d) EL spectra of FF-0.25 and PFH-FF at 8V.

FF-25 with almost same color (0.38, 0.44) displayed a power efficiency of 4.16 lm W^{-1}. Other copolymers with intermediate compositions namely; FF-10, FF-5 and FF-1 showed an electroluminescence with CIE coordinates of (0.30, 0.36), (0.33, 0.38) and (0.31, 0.36) respectively at 8 V (Figure 5(c)) that are very close plankian locus of CIE 1931 color space. FF-0.25 elicited a white electroluminescence with CIE coordinate of (0.30, 0.31) with a luminous efficiency of 5.17 cd A^{-1} and power efficiency of 4.12 lm W^{-1}(Table S3†).

An interesting feature observed with the FF-0.25 copolymer when the EL and PL spectra were compared. Till date the best efficiency of white single polymer based LEDs were reported for polyfluorene with napthalimide and benzothiadiazole based side chains.[54] However, the above polymer also displayed a predominant long wavelength emission in EL as compared to its PL spectra resulting in low color purity of EL. The difference between PL and EL spectra of polymers was attributed to charge trapping where the electronic levels of the covalent dopants are located within the band gap of host, polyfluorene. Such observations of charge trapping was also reported for most of the reported white light emitting single copolymers with covalent dopants in main and side chains as well.[55]

In the case of FF-0.25, FF units act as covalent dopant in complete conjugation with the main chain. The energy level diagram presented in Figure 4 (c) shows that the LUMO is stabilized by ~1.3 eV in case of all the copolymers relative to that of poly(9,9-dihexylfluorene)-2,7-diyl (PFH) due to introduction of FF units in polymer backbone. As a result the the difference between hole and electron injection barriers are reduced. In FF-0.25, the electron and hole injection barrier were found to be 0.49 eV and 0.54 eV respectively. Herein, the unique positioning of energy levels in FF resulted in almost equal charge injection barriers and consequent ambipolar property of FF-0.25. The low dipole moment of FF units on the other hand as observed earlier resulted in reduced charge transfer states and dominant emissive states. A turn on voltage of 4.1 V and maximum brightness of 9106 cd/m^2 was observed for OLED with FF-0.25 as emissive layer at applied voltage of 10.5 V. A luminous power efficiency of 4.12 lm W^{-1} and external quantum efficiency of 3.10% was observed at brightness of 1000 cd m^{-2}. Data on OLEDs fabricated from other OLEDs are presented in Table S3†.

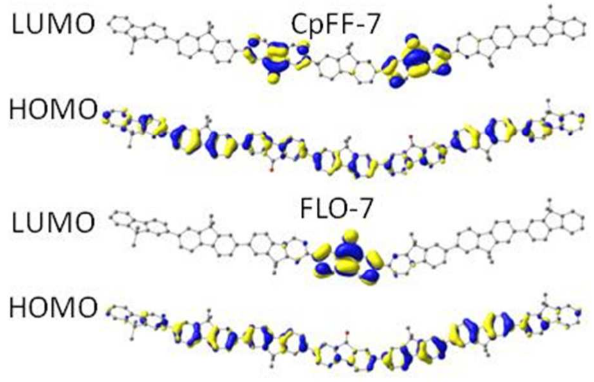


Figure 6. Structures and spatial distribution of HOMO and LUMO in model systems.

Table 2. Parameters from theoretical calculations[e]

systems	[a] ΔE_{IP-EA}	[b] E_1	[c] E_b	[d] λ_h	[d] λ_e
CpFF-7	2.96	2.45	1.80	0.10	0.14
FLO-7	2.90	2.44	1.96	0.10	0.16

[a] ΔE_{IP-EA}, difference between ionozational potential and electron affinity; [b] E_1, first singlet excitation energies; [c] E_b, exciton binding energies; [d] hole (λ_h) and electron (λ_e) reorganization energies; [e] all units of energies are in eV.

Ambipolar charge injection results in voltage independent output of LEDs, the output of white light emitting diodes were study for their spectral stability. The OLED fabricated with FF-0.25 as emissive layer showed a very stable spectrum with no change in relative intensity of long and short wavelength emissions as shown in Figure 5(b). In order to understand the EL property of FF-0.25 copolymer with white light emission, OLEDs with blend of PFH and FF in same composition (0.25%) was prepared and studied. EL spectrum of blend with same composition, PFH-FF showed predominantly long wavelength emission centered at ~560 nm with CIE coordinates of (0.38.0.43) at 8 V (Figure 5 (d)). The EL observed the blend, PFH-FF is characteristic of FF emission. The long wavelength emission can be attributed to inhomogenity in the thin film of the blend, PFH-FF leading to trapping of charge carriers in FF even at low compositions. Thus the single copolymer, FF-0.25 showed better electroluminescent properties with no surplus long wavelength emission than the corresponding blend and previously reported single polymers. The copolymer FF-0.25 also elicited a good fluorescence stability in THF solution at different temperatures (Figure S6†).

Theoretical studies on copolymer

Density functional theory (DFT) calculations have been employed to understand the electronic structure of the polymers, such as frontier molecular orbitals (FMO) and orbitals involve in the dominant excited state transition. Model systems of FF copolymers (CpFF-7) and polymers with single fluorenone unit (FLO-7) were constructed as shown in Figure 6. The FMO distribution clearly showed that HOMO of the model oligomer of FF (CpFF-7) is delocalized over the entire molecule (Figure 6), on the other hand the LUMO is localized only on the fluorenone unit. It reveals that the intramolecular charge transfer takes place from the fluorene to fluorenone moiety. Similarly in the case of model system with single fluorenone moiety (FLO-7), the HOMO is delocalized on the entire molecule while LUMO is concentrated only on the fluorenone unit. TD-DFT calculations on the model systems, CpFF-7 and FLO-7 showed that lowest energy absorption corresponded to HOMO→LUMO transition and calculated absorption values were consistence with experiment (Table S5†).

To achieve high ratio of maximum quantum efficiencies of electroluminescence (EL) to photoluminescence (PL) the binding energy of electron–hole (exciton) pair needs to be sufficiently low.[56] Typically, the E_b corresponds to the difference between the optical and fundamental band gaps.[57] Theoretically, E_b is calculated by using the following equation (1).[57]

$$E_b = E_{fund} - E_{opt} = \Delta E_{IP\text{-}EA} - E_1 \qquad (1)$$

E_{fund} is the fundamental gap and can be approximated as the energy difference between ionization potential (IP) and electron affinity (EA) ($\Delta E_{IP\text{-}EA}$), while E_{opt} represents the optical gap and is generally defined as the first singlet excitation energy (E_1) obtained from the TD-DFT calculation. From the Table 2, it is clear that, the FF containing model system, CpFF-7 had lower E_b (1.80 eV) than the FLO-7 (1.96 eV). Hence, the FF copolymers can be expected to efficiently form the excitons within the emissive layer. In π-conjugated organic electronic materials, charge motion occurs predominantly by a hopping-type mechanism where charge transport property described by the incoherent hopping model,[58] by means of standard Marcus equation[59] governed by reorganization energy. The reorganization energies were evaluated by the adiabatic potential-energy surface approach described in detail in previous studies.[60] In order to evaluate the charge mobility, the reorganization energies of the polymers were evaluated (Table 2). The reorganization energy provides a qualitative indication of the charge carrier mobility with low reorganization energies being associated with higher transport rate of the carriers. The calculated hole (λ_h) and electron (λ_e) reorganization energies of CpFF-7 and FLO-7indicate a balanced charge transport in CpFF-7 as the reorganization energies for their hole and electron are comparable (with difference, $\Delta\lambda$=0.04 eV). Thus, the better performance of the copolymers of FF can be attributed to the ambipolar charge carrier mobility leading to efficient confinement of excitons in emissive layer.

Conclusions

A series of copolymers of 9,9-Dihexylfluorene and 2,7-bis(9H-fluoren-9-one-2yl)-9,9-dihelylfluorene (FF)were designed. These copolymers exhibited enhanced emission even at very low proportion of 0.25% compared 10% previously reported for Tetraphenylethylene-fluorene copolymers.[47] A white light emission was realized in single copolymer (FF-0.25) of a AIEE luminogen. LEDs fabricated with a device configuration of ITO/PEDOT:PSS/Polymer/Al with FF-0.25 as emissive layer displayed a EL with CIE coordinates of (0.30, 0.31) that was very close to white light emission with maximum brightness of 9106 cdm^{-2} and power efficiency of 4.12 lm W^{-1}. Further the EL spectra of FF-0.25 showed no surplus long wavelength emission compared to the PL indicating energy transfer to be the dominant process in white electroluminescence in contrast to previous reports on single copolymers even with an additional electron injection layer.[61] A combination of ambipolar property with AIE was already demonstrated to be beneficial for blue OLED albeit in a multilayer architecture.[62] However, this work opens a new approach where AIEE and ambipolar charge injection can be combined for single polymer white light emitting diodes through solution processing in simple device configuration.

Experimental Section

UV-Visible absorption studies were carried out on Varian Carey 50 Bio UV-Visible spectrophotometer and emission spectra were done Varian Carey Eclipse spectrophotometer . The absorption and emission studies were carried out using solutions with concentration of 5x10^{-4} g dl^{-1}. The thin film spectral properties were studied using spun thin films on optically clean quartz substrates with ~1mm thickness prepared from solutions with concentration of 2 mg ml^{-1}. DLS experiments were carried out on Dynamic Light Scattering instrument from Malvern instruments, UK. FLT experiments were done on IBH fluorescence life time instrument with picoseconds resolution and data analyses were done using Horiba Jobin Vyon decay analysis program. For both DLS and FLT studies, the concentrations of solutions used were same as that used for absorption and emission studies (5x10^{-4} g dl^{-1}). Atomic force micrographs were obtained on Nova 1.0.26 RC1 Atomic force microscope with NT-MDT solver software for analysis, Silicon cantilever (SII) with average frequency of 260-630 kHz with force constant of 28-91 N m^{-1} were used in semi contact mode.

GIXRD studies of thin films of polymers coated on ITO substrate using Bruker AXS D8 Advance X-ray diffractometer with Cu Kα wave length. Absolute fluorescence quantum yield of polymer thin films drop cast on glass substrates were measured using FLUOROLOG3 (model FL3-II) fluorescence spectrophotometer from JOBIN YVON-SPEX instruments. S.A.Inc, USA, equipped with integrated sphere.

OLEDs of polymers were fabricated by spin coating PEDOT:PSS (60-100nm) solution on plasma cleaned ITO substrate. The PEDOTE:PSS coated ITO (110nm and 10 Ω/square) substrates were baked at 200 ˚C for three hours. After the above process 300µl of polymer solutions with 1mg /1ml concentration in chloroform were spin coated at 2000 rpm for 60 seconds to get uniform films of polymers with thickness of 100-130nm. Following the coating of polymers aluminum was coated at 10-5 torr. Luminescence-Voltage (L-V) characteristics of OLEDs were studied using Nucleonix type PT 168 PMT housing with drawer assembly. Current-Voltage (I-V) characteristics were studied on Kiethley 2400 source meter. Electroluminescence spectra of OLEDs were recorded in Carey Eclipse fluorescence spectrophotometer with chemiluminescence mode. Color coordinates of the LEDs and thinfilms were determined using Konica Minolta CS-100 Chroma meter in automated mode.

All the calculations were carried out using Gaussian 09 program package.[63] Further details of methods used theoretical calculations are presented in Supplementary Information. †

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Notes and references

[a] *Council of Scientific and Industrial Research (CSIR)-CLRI,Adyar, Chennai – 600 020, Fax: +91-044-24911589; Tel: +91-044-24437189; E-mail: nsomanathan@rediffmail.com, somanathan@clri.res.in.*
[b] *CSIR-Network of Institutes for Solar Energy, India.*
[c] *Academy of Scientific and Innovative Research (AcSIR), Anusandhan Bahavan, 2 Rafi Marg, New Delhi 110001, India.*
[d] *Photosciences and photonics, CSIR – National Institute for Interdisciplinary Science and Technology (NIIST), Council of Scientific and Industrial Research(CSIR), Thiruvananthapuram – 695 019, India.*

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Graphical Abstract

An AIEE luminogen is used as covalent dopant in a single copolymer with white light emission. The copolymer based of AIEE luminogen showed ambipolar charge injection and minimized charge trapping leading to stable white electroluminescence.