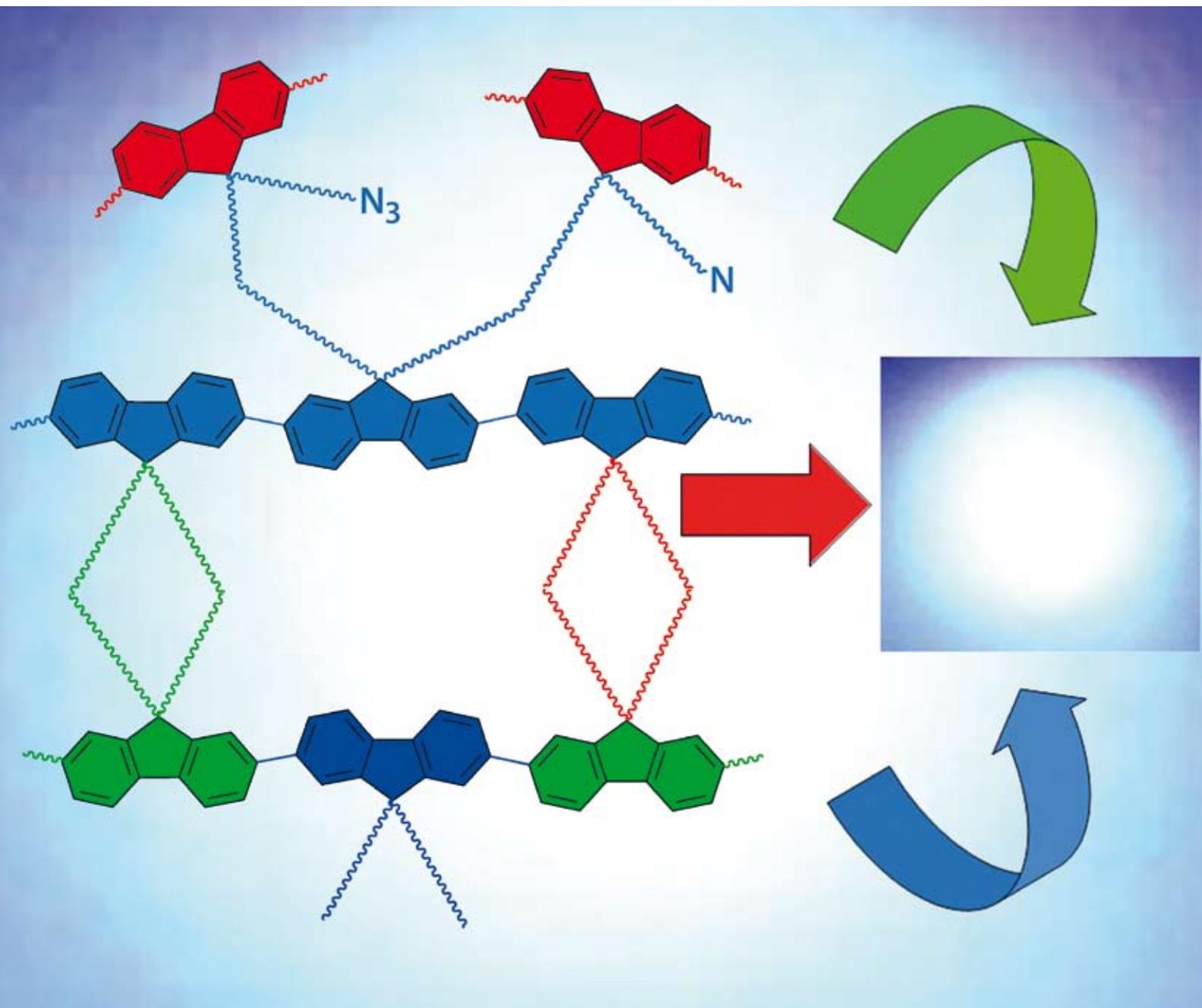


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PAPER

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On the origin of high quality white light emission from a hybrid organic/inorganic light emitting diode using azide functionalized polyfluorene

HIGHLIGHT

Francisco Zaera
The surface chemistry of thin film atomic layer deposition (ALD) processes for electronic device manufacturing

On the origin of high quality white light emission from a hybrid organic/inorganic light emitting diode using azide functionalized polyfluorene†

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High quality white light generation with high colour rendering index (CRI) was achieved by integrating a cross-linkable azide functionalized polyfluorene derivative, namely poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-azidoethyl)fluorene)] (PFA), as a down-converting fluorescent material on the inorganic n-UV InGaN/GaN LED platform. For comparison, two other polyfluorene based polymers, namely poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-bromoethyl)fluorene)] (PFB) and poly[9,9-dihexyl-9H-fluorene] (PF), were tested for white light generation. While PFA and PF both led to white light generation, PFB fell out of the white region on the chromaticity diagram. Compared to PFA, both of the control groups (PF and PFB) exhibited much lower CRI. To gain a better insight into the mechanisms playing a key role for the generation of such high quality white light in PFA, all of these polymers were further subjected to a series of experiments such as controlled exposure to heat at 220 °C for 2 h under Ar and in air. The polymers PFA and PFB, which include cross-linkable groups, produced broad emission spectra in the region of 430–650 nm upon annealing in the absence of oxygen under Ar atmosphere while almost no change was observed in the emission spectrum of PF without any cross-linkable groups. PFA undergoes cross-linking through the decomposition of azide leading to reactive nitrene species, whereas in PFB cross-linking probably occurs *via* debromination. This result clearly proved that the broadening can not be attributed only to photo or thermal oxidation, but it is also due to cross-linking. PFA was also exposed to n-UV light from the InGaN/GaN LED to investigate its photostability. In these experiments, the spectral changes in absorbance and emission properties and thermal transitions of these polymers were monitored by FT-IR, UV-Vis and fluorescent spectrometry, and differential scanning calorimetry (DSC). These experiments indicated that PFA provides high quality white light opportunely *via* cross-linking and remains stable once cross-linking is formed in a solid film.

Introduction

An increasing awareness of the necessity to save energy has directed scientific research to develop various energy-saving materials and techniques for use in displays and lighting applications. In this context, white light-emitting diodes (WLEDs) promise great potential to replace the traditional incandescent white light sources because of their significant economical and technological advantages in energy saving.

There are a number of approaches for the generation of white light. Among them, the strategies involving wavelength converting WLEDs and white emitting polymer diodes are more commonly used.^{1–5} Different photoemitters such as phosphors,^{6,7} nanocrystals,^{8–11} polymers,² and hybrid nanocrystals/polymer systems¹² have been used on electrically driven LEDs for the generation of white light by the wavelength conversion technique. Because of their versatility and superior optical properties,

conjugated polymers are on their way to earning an irreplaceable position for use in white light generation though phosphors have thus far been most extensively used for white light applications. Conjugated polymers possess inherent advantages over other photoemitters such as high absorption coefficients and feature high solid-state photoluminescence quantum efficiencies. Also, with conjugated polymers, an almost unlimited number of chemical modifications are possible, resulting in more easily processed, custom tailored, and functional materials. Furthermore these materials can be coated using very low-cost techniques.^{2,5} For these reasons, light emitting conjugated polymers have been explored for their potential use, for instance, in full colour displays.^{3–5,12–19} Recently, various strategies have been developed for the efficient use of those materials also as down-converting fluorescent materials on inorganic light emitting diodes or in electrically driven polymer based LEDs to generate white light.² The methods most commonly used for these purposes are listed as: 1) blending orange or red emitting organic or organometallic dyes with blue emitting host polymer; 2) employing a single polymer in which the different blue, green, and orange/red emitters are connected to polymer main chain covalently; and 3) the dopant/host strategy in which small amounts of green or red fluorescent dyes are grafted onto the side chain of a blue emitting polymeric host to form an

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† Electronic supplementary information (ESI) available: Experimental details, ¹H-NMR spectra, device fabrication details, and photometric properties. See DOI: 10.1039/b802910e

intramolecular dopant/host system.^{14–19} Due to the complexity of multi-chromophore polymers or blend systems there arises some difficulty in the formation of uniform multiple polymer films which can be attributed to the intrinsic phase separations among different components in the system.^{2,3} It is also difficult to synthesize such multi-chromophore polymers in high yields. Aside from the disadvantages encountered in these approaches, which are mainly related to the physical behaviour or the preparation method of the polymers, there exist also some constraints in terms of optical performance. For example, it has been difficult to obtain a very high colour rendering index (CRI), which is required to be >80 for future solid-state lighting applications.²⁰ Also, alternative to polymer blend systems and multi-chromophore polymers, the use of a single type of polymer would reduce energy losses associated with the emission and re-excitation of several chromophores, which would in turn result in much higher fluorescence quantum efficiencies.

The generation of white light based only on a single type of simple polymer emitters with high colour rendering index and high fluorescence quantum efficiency would be highly desirable. To this end, recently we have reported the white light generation ability of azide functionalized polyfluorene (poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-azidoheptyl)fluorene)], PFA) by its hybridization on an InGaN/GaN based n-UV LED.²¹ The integration of the single PFA layer onto the inorganic n-UV LED platform enabled the generation of high quality white light with colour rendering index as high as 91. We also reported on the high fluorescence quantum efficiency of PFA which we used for the preparation of hybrid organic/inorganic devices. The fluorescence quantum yield of the PFA solution was recorded to be as high as 0.86. However, the origin of the high quality white light generation of PFA has not been previously investigated and a comparative study has not been conducted. In this work, two other polyfluorene based polymers, namely poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-bromoheptyl)fluorene)] (PFB) and poly[9,9-dihexyl-9H-fluorene] (PF), were also tested as control groups for white light generation to understand better the mechanisms for the generation of such high quality white light in PFA. For comparison, these three polymers were subjected to a series of experiments such as controlled exposure to heat at 220 °C for 2 h under argon and in air. They were also exposed to

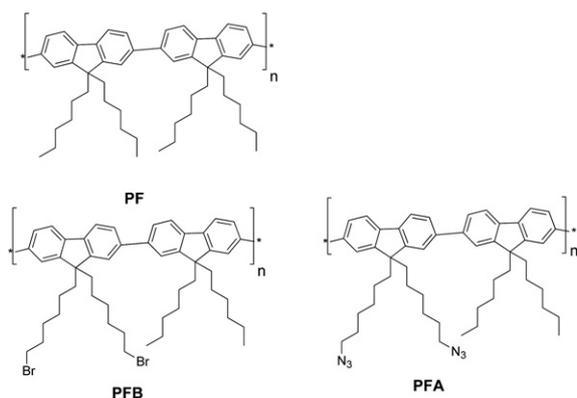


Fig. 1 Structures of poly[9,9-dihexyl-9H-fluorene] (PF), poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-bromoheptyl)fluorene)] (PFB) and poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-azidoheptyl)fluorene)] (PFA).

n-UV light from the InGaN/GaN LED to investigate their photostability. The spectral changes in absorbance and emission properties of these polymers were monitored by FT-IR, UV-Vis and fluorescent spectrometers. Also, thermal changes taking place during heating of the polymers were investigated by differential scanning calorimetry (DSC). These experiments indicated that PFA provides high quality white light opportunely *via* cross-linking up to a certain degree and remains stable once a partially cross-linked network is formed in a solid film. The PFA hybridized devices lead to the generation of a very broad down-converting fluorescence across the entirety of the visible spectrum upon pumping of the PFA emitters at 387 nm by our electrically driven n-UV InGaN/GaN LED.

Results and discussion

Syntheses and characterization of polymers

Poly[9,9-dihexyl-9H-fluorene] (PF) was synthesized by the Suzuki coupling of 2,7-dibromo-9,9-dihexyl-9H-fluorene with 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) in 64% yield. Following the synthesis of poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-bromoheptyl)fluorene)]²² (PFB) using Suzuki coupling conditions, the bromide groups were converted into azide by nucleophilic substitution reaction using sodium azide in DMF. Poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-azidoheptyl)fluorene)] (PFA) was obtained in 75% yield.

The conversion of the bromide groups into azide was verified by ¹H-NMR and FT-IR spectroscopy. The upfield-shifted peak of methylene protons adjacent to azide from 3.32 ppm to 3.17 ppm was observed in the ¹H-NMR spectrum upon the conversion of bromide to azide. Similarly, the conversion of bromide to azide in PFA was confirmed by the characteristic azide bond stretching at 2094 cm⁻¹ observed by FT-IR. The weight average molecular weights (M_w) of PFB and PFA were determined as 2.04×10^4 g mol⁻¹ for both by gel permeation chromatography (GPC) using polystyrene as standard. The result indicates that no cross-linking occurred during the conversion of bromides to azide groups.

Photophysical properties

Absorption and fluorescence emission spectra for the three polymers were recorded in THF solution and in thin films coated on double-side polished fused silica. Fig. 2 represents the absorption and fluorescence spectra of each in their solution and film states. The fluorescence emissions of all three polymers are separated sufficiently far from their absorption edges so that self-absorption is almost negligible, which facilitates a larger overall efficiency of the resulting hybrid devices. The fluorescence quantum yields recorded in solution for PFA, PFB and PF were 0.86, 0.88 and 0.83 respectively with quinine sulfate used as the standard. PFA and PF are quite similar in that these polymers have the tendency to broaden their fluorescence emission when in their film states. This spectral broadening can be assigned specifically to a wide region in the visible range spanning from 420 nm to 650 nm, whereas a broadening is not prevailing in the case of PFB as it turns from solution into its film state. The electron withdrawing bromide groups added to the side chains of PFB lead probably to a decrease in intermolecular interactions of

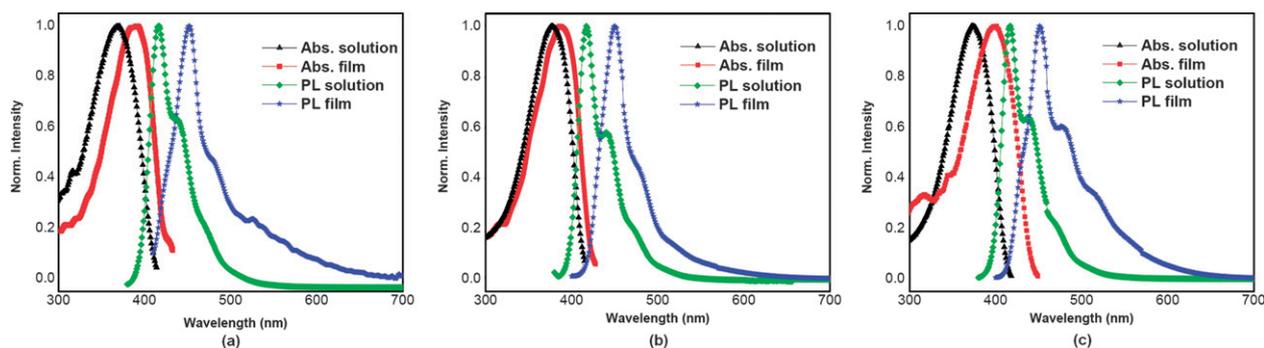


Fig. 2 The absorption and fluorescence spectra of (a) PFA, (b) PFB, and (c) PF in THF and thin film.

the conjugated backbone and also aid as bulky groups preventing physical aggregate formation. The changes in full-width at half-maximum (FWHM) values of the first peak, being centred at approximately 417 nm in solution and 450 nm in film, and the shoulder at 470 nm in solution and 520 nm in film, are depicted in Table 1. We expect inherently a spectral broadening upon film formation as a result of the increasing stacking interactions among polymer chains. Indeed, the FWHM of all three polymers increase at least 10 nm for λ_1 and 34 nm for λ_2 . The reason that PF broadened more than PFB is probably due to the absence of any bulky group positioned on the side chain, which would help physically the prevention of intermolecular interactions. Though PFA has such an extra group ($-N_3$), these aid the cross-linking mechanism at a low degree upon film formation and further increase the cross-linked portions within the polymer upon heating at temperatures in the range from 170–280 °C.^{23–28}

Thermal properties

Thermal investigations leading to further insight into the processes taking place at higher temperatures were performed by differential scanning calorimetry measurements. The measurements were driven from 30 °C up to 400 °C. The endothermic peaks at approximately 60–70 °C in the DSC curves of PFA and PFB in Fig. 3 indicate the glass transition temperatures to be within the range of 60–70 °C. PFA exhibits a highly exothermic peak at 218 °C which seems to depend exclusively on cross-linking as deduced from the presence of the highly cross-linkable azide groups on the hexyl side chains.²³ Though the cross-linking mechanism starts even at room temperature upon film formation

Table 1 Optical transition peak wavelengths and corresponding FWHM of PFA, PFB and PF (given in nanometers)

	PFA		PFB		PF	
	Wavelength	FWHM ^a	Wavelength	FWHM ^a	Wavelength	FWHM ^a
Solution						
λ_1	417	18.7	417	18.0	417	17.3
λ_2	466	22.3	471	24.1	471	26.9
Film						
λ_1	452	36.0	449	27.3	450	29.1
λ_2	524	139.3	517	58.4	518	70.5

^a The FWHM values were evaluated *via* the Lorentzian fit method.

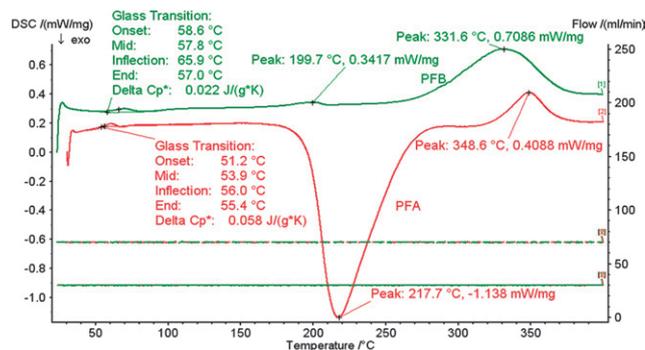


Fig. 3 DSC analyses of PFA and PFB. The exothermic peak of PFA centred at 218 °C indicates the cross-linking mechanisms taking place as highly reactive nitrene species insert into side chains or polymer backbone.

probably induced by daylight,²⁴ at temperatures starting from 170 °C the side chains lose essentially all of their $-N_3$ end groups to form networked structures by the insertion of highly reactive nitrene species. This exothermic process produces heat at a rate of 1.138 mW mg⁻¹. For PFB, we observe only a minor endothermic peak at 200 °C with heating at a rate of 0.342 mW mg⁻¹. Upon heating PFB loses Br probably by producing alkyl radicals, which combine with other side chains to form a cross-linked polymer. Since the endothermic process in PFB is probably compensated by an almost equally exothermic process, we are able only to observe the endothermic process. Decomposition of both polymers PFB and PFA takes place at temperatures starting from 270 °C and 300 °C, respectively. This shows that PFA forming a highly networked structure has higher resistance towards decomposition. PFB may start to decompose earlier since some chains would still have not cross-linked at the same temperature.

A comparative study revealing the emission properties of three polymers PF, PFB, and PFA on an inorganic platform was performed using an InGaN/GaN based n-UV LED as the pumping source for the excitation of these organic light emitters at 378 nm. Absorption of the excitation energy leads to a quite broad down-converted photoluminescence which is especially useful for the generation of white light for both PF and PFA, but not for PFB. While the tristimulus coordinates of both PF and PFA at around (0.3, 0.3) fall in the white region of the CIE diagram, those of PFB (0.2, 0.1) remain in the blue region. The

quantitative criterion that determines and distinguishes between the quality of the generated white light for PF and PFA is the colour rendering index. PFA reaches a CRI of 91, which is sufficiently high to make it the future material of choice.¹ Though the tristimulus coordinates of PF are also quite well positioned in the white region, its CRI of 78 is lower. (Table S1 depicts the tristimulus coordinates, CRI, and colour temperature (T_c) of these three polymers in ESI.†)

Investigation of the origin of white light emission in the azide functionalized polyfluorene

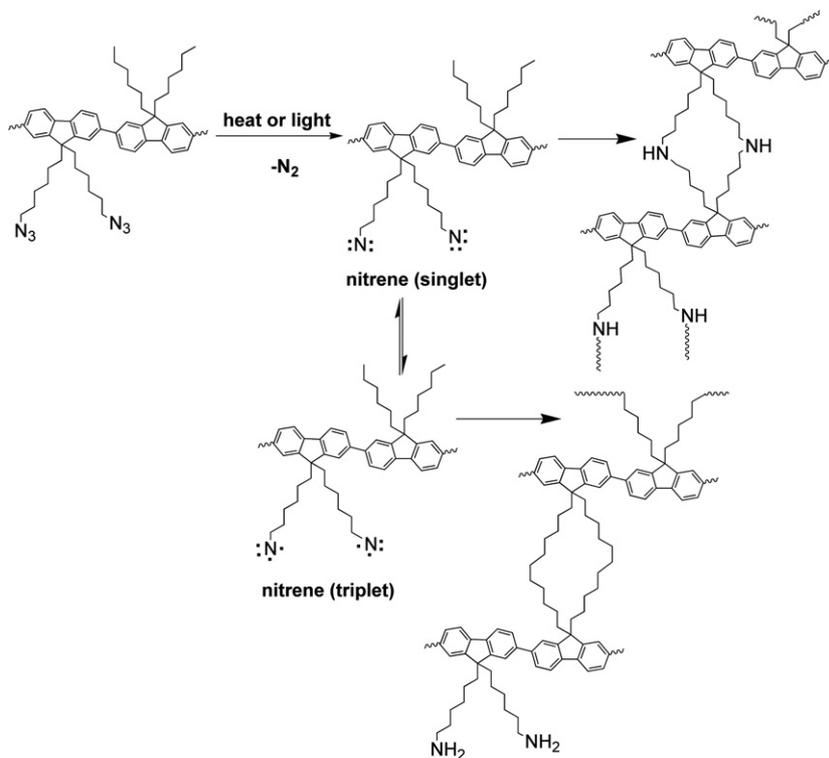
High quality white light from PFA was obtained as a result of its spectral broadening ability through the entirety of the visible range as was confirmed by the highest and largest increase in the FWHM of the shoulder around 520 nm upon film formation. This broadening is induced by the cross-linking mechanism of azide groups even at room temperature though maintained at a considerably low level.²⁴ Although a broadening of the emission spectrum is undesired especially for light emitters intended to emit at specific wavelengths as in display applications; this disadvantage is turned into an advantage by making direct use of the wide spectrum ranging from 420 nm to 650 nm for the generation of white light with impressive CRI values as high as 91. We believe that this feature originates from the azide group attached to the side chains of the polyfluorene backbone, which is responsible for the cross-linking mechanism of this polymer.

It is known that an azide first decomposes to a highly reactive nitrene species with the loss of nitrogen on heating or irradiation

by UV light^{23–28} or even as recently reported under daylight slowly.²⁴ However, the fate of the nitrenes formed during thermal or photochemical cross-linking is not exactly known. The nitrene can be in a singlet or triplet (diradical) state and stabilize itself *via* various mechanisms by abstracting available protons or by inserting into single or double bonds, and onto other side chains or the polymer backbone of different polymer chains. Scheme 1 shows some possible mechanisms for the cross-linking of azide containing polyfluorene.

To obtain some detailed information about the mechanisms taking place during the operation of the PFA-hybridized device, we carried out a series of experiments along with the control groups PF and PFB with and without the n-UV LED. First, the decomposition of azide groups was observed in a controlled manner by *in-situ* heating of a thin PFA film with FT-IR spectroscopy in air (Fig. 4).

The thin films of the polymers were prepared by drop casting their THF solutions on silicon substrates for FT-IR analysis. PFA was gradually heated under air starting from 25 °C to 230 °C, where the characteristic azide stretching band at 2094 cm^{-1} has almost completely disappeared. If we closely inspect the IR spectra of PFA before and after cross-linking, one can see that the intensity of the peak at 3200–3400 cm^{-1} increased and a new weak peak at 1230 cm^{-1} appeared probably due to formation of NH and C–N bonds respectively during cross-linking. Noticeably important is, on the other hand, a very weak peak at 1720 cm^{-1} , which becomes apparent at relatively high temperatures of about 220 °C. This peak can be attributed to the carbonyl of the fluorenone formation in the polymer chain.



Scheme 1 Decomposition of azides under light or heat to produce nitrene which can be in singlet or triplet states. Each states react differently; singlet nitrene undergoes insertion while triplet (diradical) nitrene abstracts available protons by producing radicals which will combine with other radicals to form a cross-linked polymer.

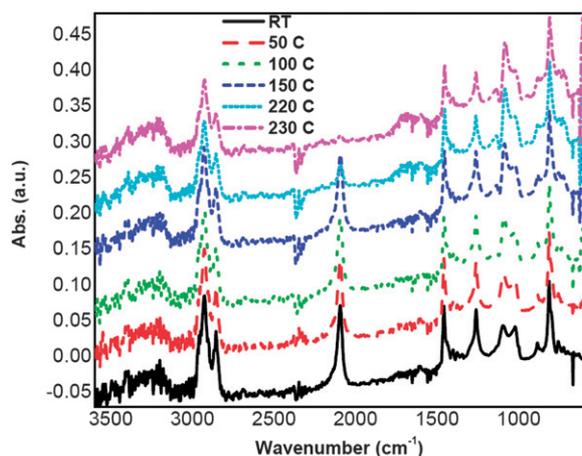


Fig. 4 *In-situ* FT-IR measurement of PFA under heat exposure.

We tried to dissolve the cross-linked film in various solvents in order to gain better insight into its structure by taking its NMR spectra, however, it was found to be completely insoluble in any solvent.

The ability of azide functionalized polyfluorene to exhibit a broad spectrum across the entirety of the visible range by cross-linkable reacting species is verified after a thorough investigation of PF, PFB, and PFA by annealing them separately in two sets for 2 h at 220 °C in air and under argon atmosphere. Fig. 5 clearly illustrates essential differences among samples heated under air and argon as well as substantial differences among three differently functionalized polymers PF, PFB and PFA. On the same figure, there are also depicted changes in the absorption spectra, where heating of the polymer films in general results in broadened and red-shifted peaks. The very intense green emission of PFA peaking at 550 nm upon heating at 220 °C for two hours is strong evidence for a structural change in the backbone, which is presumably attributed to cross-linking. Additionally, in the presence of air this green emission further red-shifts for several nanometers as a result of keto defect formation.^{29–33} Under argon PFB similarly shows a green emission albeit to a lesser degree than PFA, supporting the fact that its bromide groups also aid the cross-linking of the polymer chains. The evidence that we observe first an endothermic peak at 200 °C from the DSC thermogram in Fig. 3, suggests that heating of PFB results first in debromination leaving reactive alkyl radicals which combine with other side chains to form a cross-linked polymer; this alters the structure of the backbone as verified by the red-shifted peak on the emission spectra of heated PFB samples. An enhancement of the red-shifted component is also observed for PFB when the film is exposed to air during heating. Nevertheless, almost no green component is observed for PF upon heat treatment under argon, which consolidates our conjecture of the effect of cross-linkable groups on the emission properties of the polymers. This effect is observed in a positive manner for PFA for the generation of white light, while it is less important for PFB since it shows up after heat treatment for a longer time.

The interesting results, obtained from controlled measurements of heat treatment on copolymers with different side chains under air and argon, disclose some distinctive properties aided by

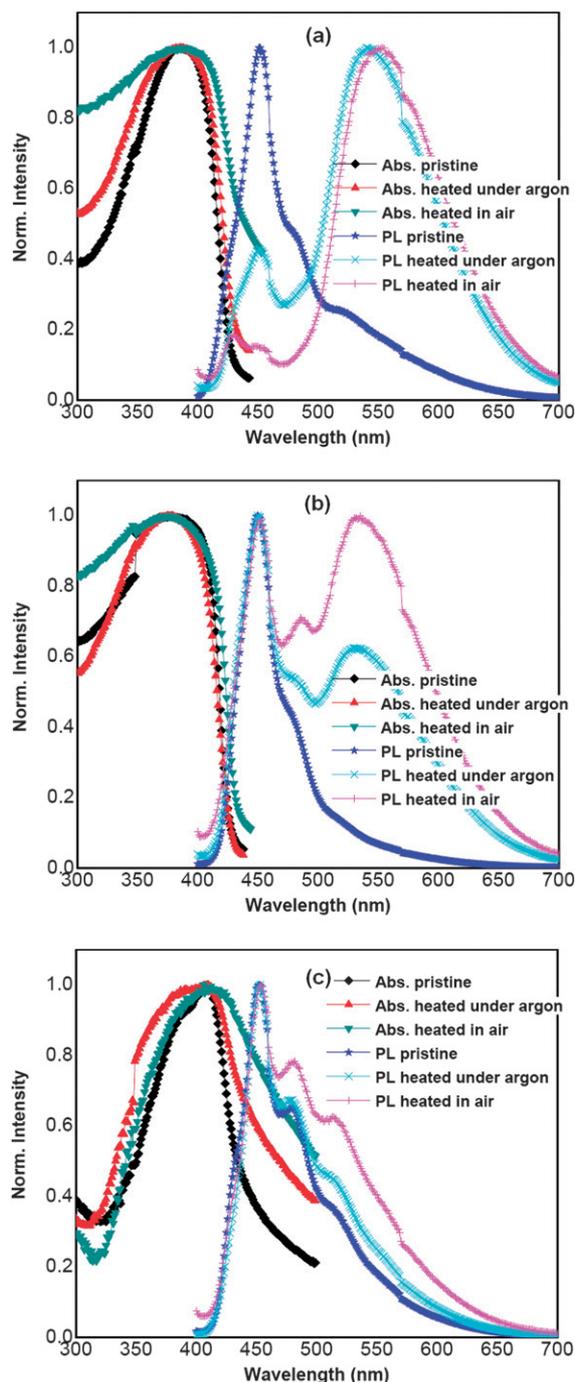


Fig. 5 Normalized absorption and PL spectra of (a) PFA, (b) PFB and (c) PF annealed at 220 °C for 2 h under argon and in air.

harsh heating treatment conditions for several hours. Indeed, these results show quite different behaviour compared to the effects observed previously on fluorene-based polymers, which are reported to possess red-shifting spectra mainly due to oxidative degradation after such treatment.^{29–34} Our polymers, except PF, contain extra cross-linking groups, which are able to supplement the emission spectra with some red-shifted component in a positive manner when kept at a controlled level. This additional contribution on the red side of the visible spectrum is

proven to be not only because of oxidative keto defect formation, but mainly due to the cross-linkable azide and bromide species on PFA and PFB, respectively.^{32,33} This, on the other hand, turns out to be beneficial for white light generation with azide group functionalisation in our case here. Additional measurements on our n-UV InGaN/GaN based LEDs for the exploration of the emissive properties of the polymers showed that at normal operation conditions almost no degradation is observed even after several hours (Fig. 6). However, one may also consider the fact that these conditions supplied by the n-UV LED are still far from the ideally proposed ones for commercially available LEDs. Upon increasing UV radiation of the n-UV LED hybrid

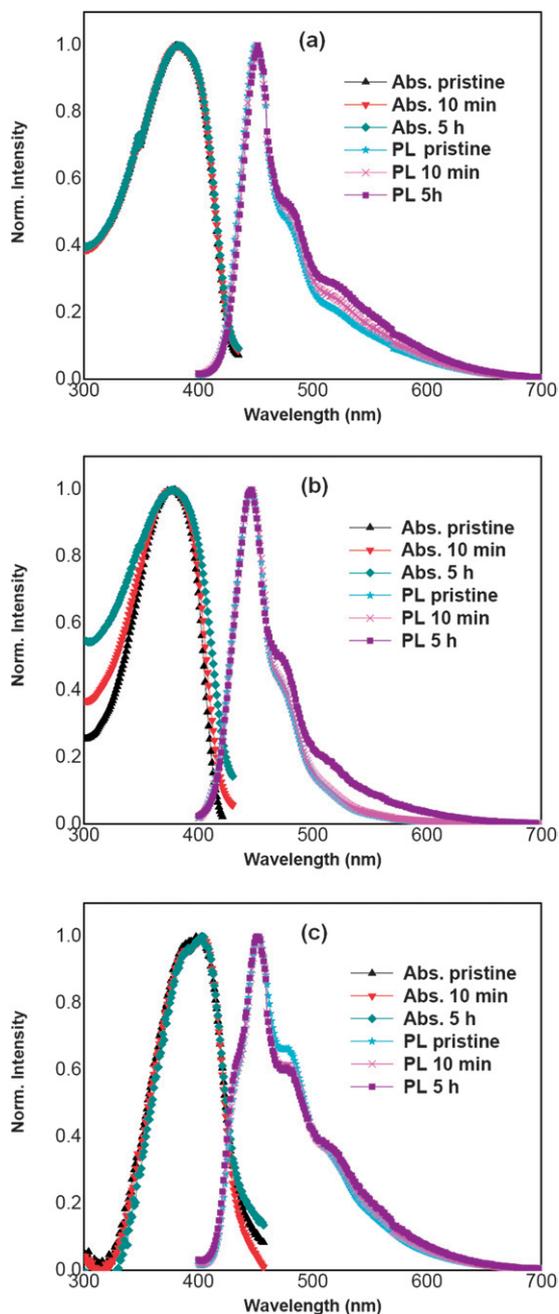


Fig. 6 Determination of the spectral stability of (a) PFA, (b) PFB, and (c) PF after UV irradiation on n-UV LED operated at 0.9 mA at 10 V.

platform operated in total for 5 h at 0.9 mA and 10 V, we observed first a slight increase in the green component at approximately 524 nm for PFA after 10 min as a result of cross-linking. For PFB, the emission curve after 10 min is however almost identical to that of the pristine film since for cross-linking to take place first the debromination should have occurred at temperatures of about 200 °C. Therefore, we observe only a significant contribution of the green emission after 5 h of device operation, in which to some extent the cross-linking processes have taken place. Similarly, there is also an increase in the green component of the PFA spectrum after 5 h. The changes observed for PFA as well as PFB demonstrate the effects of cross-linkable species for yielding better (x, y) tristimulus coordinates and higher CRI, required for the generation of high quality white light. Even though PF, the polymer which does not possess any labile group on its side chains, is subjected to some degradative conditions it does not show a noteworthy change in its spectrum except a slight decrease in intensity which has also been observed for PFA and PFB. This property evidences clearly the fact that under these operation conditions our polymers are hardly affected by oxidative degradation processes; instead cross-linkable groups on PFA and PFB take control over the emissive properties of our polymers. Since the CRI of PF is not as high, though it possesses a relatively well-oriented position in the white region of the CIE diagram, it is quite advantageous to control the cross-linking mechanisms of PFA up to a certain level to obtain a high CRI for the fulfilment of the major requirement to get high quality white light.

In addition, we analyzed our PFA hybridized LED at different current injection levels (Fig. 7). This shows again that the labile azide group undergoes some reactions through the formation of some reactive nitrene species. Though PFA is a good candidate as it is for future high quality white light generation, one may still consider further modifying the emissive properties of PFA by tailoring certain spectral changes, playing with some parameters such as heat or UV radiation exposure. This may aid a sufficient increase in the red component of the visible spectrum, which could enhance the performance of the white light emitting device.

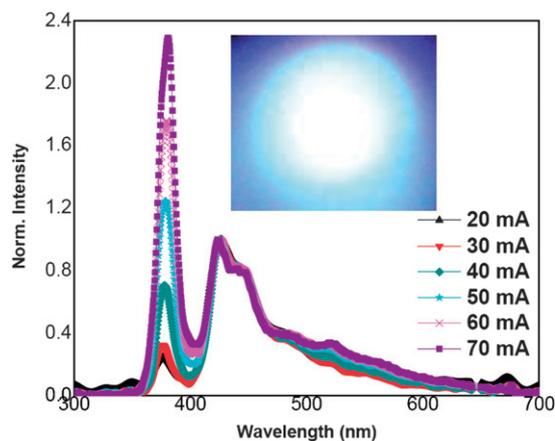


Fig. 7 Spectral behaviour of PFA hybridized on n-UV InGaN/GaN based LED at different current injection levels. The spectra are normalized according to the peak at 425 nm.

Conclusions

In this work, we reported on the origin of high quality white light generation by the hybridization of a single and simple azide-functionalized polyfluorene derivative, namely poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-azidohexyl)fluorene)] (PFA) with an InGaN based n-UV LED. The integration of the organic film onto the inorganic n-UV LED platform enabled the generation of high quality white light with CRI values as high as 91, with the use of the single polymer PFA. Our PFA based hybrid device allows the generation of a very broad down-converting photoluminescence across the whole visible spectrum when the PFA emitters are pumped at 378 nm by the electrically driven n-UV InGaN/GaN LED. Also, as control groups two similar polyfluorene derivatives, poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis(6-bromohexyl)fluorene)] (PFB) and poly[9,9-dihexyl-9H-fluorene] (PF) were used for a comparative study. To investigate further the origin of white light generation from PFA, these polymers were studied under controlled exposure to heat at 220 °C for 2 h under argon and air atmospheres. The polymers PFA and PFB, which include cross-linkable groups, produced broad emission spectra in the region of 430–650 nm upon annealing in the absence of oxygen under Ar atmosphere while almost no change was observed in the emission spectrum of PF without any cross-linkable group. PFA undergoes cross-linking through the decomposition of azide leading to reactive nitrene species, whereas in PFB potentially cross-linking is caused by debromination leading to alkyl radicals. This result clearly proved that the broadening can not be attributed only to photo- or thermal oxidation, but it is also due to cross-linking. PFA was also exposed to n-UV light of the InGaN/GaN LED to investigate its photostability. The spectral changes in absorbance and emission properties of the polymers were monitored by UV-Vis and fluorescent spectrometry. The thermally induced decomposition of azides leading to cross-linking was monitored by FT-IR *in situ*, and DSC. These experiments indicated that PFA provides high quality white light opportunely *via* cross-linking and remains stable once cross-linking is formed in solid film.

Acknowledgements

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