

White emitting polyfluorene functionalized with azide hybridized on near-UV light emitting diode for high color rendering index

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Abstract: We develop and demonstrate high-quality white light generation that relies on the use of a single-type simple conjugated polymer of polyfluorene functionalized with azide groups (PFA) integrated on a near-UV LED platform. The high-quality white emission from the polyfluorene is achieved by using the azide functionalization to facilitate cross-linking intentionally when cast into solid-state form. Hybridized on n-UV InGaN/GaN LED at 378 nm, the PFA emitters collectively generate a very broad down-converting photoluminescence at longer wavelengths across the entirety of the visible spectrum, yielding high color rendering indices up to 91.

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29. PFB, bromide functionalized polyfluorene, poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis-(6-bromohexyl)fluorene)] Yield: 1.1 g, 64%. IR (KBr, cm^{-1}): 3065 (CH-), 2935 (CH-), 2859 (CH-), 1613 (C=C-), 1571 (C=C-), 727 (C-Br). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ_{H} 7.85 (m, 12H), 3.32 (t, 4H, $J=6$ Hz), 2.16 (m, 4H), 1.71 (m, 4H), 1.22 (m, 24H), 0.84 (m, 14H). Gel-permeation chromatography (GPC): $M_n = 3.87 \times 10^3$, $M_w = 2.04 \times 10^4$ (Polystyrene as standard). Fluorescence quantum yield (FQY): 0.88 (Quinine sulfate as the standard).
30. PFA, azide functionalized polyfluorene, poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis-(6-azidohexyl)fluorene)] Yield: 205 mg, 75%. IR (KBr, cm^{-1}): 3065 (CH-), 2935 (CH-), 2859 (CH-), 2100 ($-\text{N}_3$), 1613 (C=C-), 1571 (C=C-). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ_{H} 7.78 (m, 12H), 3.17 (m, 4H), 1.95 (m, 4H), 1.7 (m, 4H), 1.20 (m, 8H), 0.65 (m, 4H, f). Gel-permeation chromatography (GPC): $M_n = 3.61 \times 10^3$, $M_w = 2.04 \times 10^4$ (Polystyrene as standard). Fluorescence quantum yield (FQY): 0.86 (Quinine sulfate as the standard).
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1. Introduction

White light emitting diodes (WLEDs) hold great promise for future lighting and display applications. Today in solid-state lighting, wavelength-converting WLEDs are more commonly used than multi-chip WLEDs and monolithic WLEDs [1,2]. In the wavelength conversion technique, different photoemitters such as phosphors [1], nanocrystals [3-5], polymers [2,6-8], and nanocrystal-polymer combination [9] have been successfully used by integrating them on pump LED sources. Among them, although phosphor is currently the most widely used wavelength-converting material, polymers also offer a number of benefits that may make them attractive for use in white light generation. First, polymers exhibit high absorption coefficients and feature high solid-state photoluminescence quantum efficiencies; second, they are easily processed, molecularly engineered, and coated using very low-cost

techniques [2,8]. To this end, light emitting conjugated polymers have been extensively studied to explore their potential use, mainly in full color displays till date [6-16].

Recently, a wide range of conducting polymers have been investigated as luminescent down-converting materials to generate white light on inorganic light emitting diodes [2]. The construction of such white emitting polymer thin films is essentially based on either preparing layer-by-layer assembly of multiple polymers or blending polymers [2,6]. Similar approaches have also been successfully shown to make electrically driven polymer-based LEDs. Another method also shown in such polymer LEDs combines the emission of multiple primary colors, necessary for the full white light generation, on a single but rather complex polymer, with multiple chromophores each of which emits a primary color simultaneously [11-16]. However, in these approaches, it has been difficult to obtain very high color rendering index (CRI), which is required to be >80 for the future solid-state lighting [17]. Furthermore, there are intrinsic problems associated with these approaches in large-scale application. These problems arise from the difficulty in making such multiple layers of uniform polymer films, the intrinsic phase separations in such complex blend systems, or the complexity of synthesizing such multi-chromophore polymers. As an alternative to these approaches, using a single type of simple polymer emitters, white light generation with high color rendering index has not been demonstrated to date.

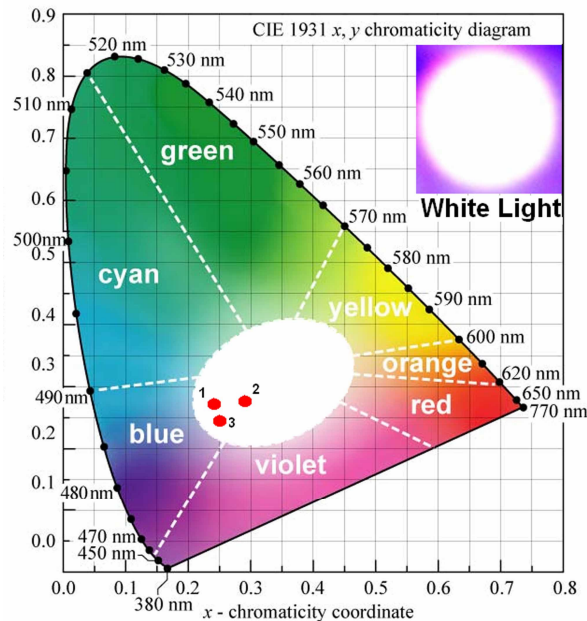


Fig. 1. White emitting azide functionalized polyfluorene hybridized on n-UV LEDs shown with three implementations operating in the white region of CIE chromaticity diagram (inset: a photograph of high-quality white light emission from PFA).

In this paper, we developed and demonstrated high-quality white light generation that relies on the use of a single-type simple conjugated polymer of polyfluorene functionalized with azide groups (namely poly[(9,9-dihexylfluorene)-*co-alt*-(9,9-bis-(6-azidohexyl)fluorene)]—PFA) that is integrated on a near-ultraviolet (n-UV) LED platform. The high-quality white emission from the polyfluorene (shown in Fig. 1) is achieved by using the azide functionalization opportunistically to facilitate cross-linking when cast into solid-state form. For the device operation, the PFA film is observed to remain stable once proper cross-linking is attained. In this approach, pumped by the n-UV InGaN/GaN LED at 378 nm, the PFA emitters collectively generate a very broad down-converting photoluminescence (PL) at longer wavelengths across the entirety of the visible spectrum, yielding high color rendering

indices up to 91. This fulfills the CRI requirement of future solid-state lighting. Furthermore, our PFA emitters exhibit high efficiency of conversion from UV pump to white emission up to 70% at room temperature. Also, the azide functionalization results in an enhancement factor of 72% (by 38 units) in CRI when compared to the control group of bromide functionalized polyfluorene (namely poly[(9,9-dihexylfluorene)-*co-alt*-(9,9-bis-(6-bromohexyl)fluorene)]—**PFB**).

Herein, we present the design, synthesis, growth, fabrication, and characterization of these hybrid white light sources. We also describe a systematic study of the optical characterization of different polyfluorenes (PFA and its control groups). In this work, we use polyfluorene based conjugated polymers (shown in Fig. 2) because of their high absorption coefficients and high solid-state photoluminescence quantum efficiencies [8,18]. Also, their structure can be conveniently modified by chemical reactions to emit across the whole visible spectrum. Furthermore, due to their good solubilities in common organic solvents they can be deposited on solid substrates using simple and inexpensive techniques such as spin coating.

2. Fabrication of hybrid polyfluorene-based organic-inorganic WLEDs

Most polyfluorene-based LEDs that are electrically driven undergo rapid degradation during device fabrication and under operation, resulting in an emission wavelength change from blue to green. Although a number of mechanisms have been suggested, the origin of the long wavelength emission remains unclear [19-22]. However, the recent results show that thermal oxidation degradation and accompanying cross-linking of polyfluorene play an important role intensifying this long wavelength emission. The cross-linking apparently enhances excitation energy migration and energy transfer to the energy traps by hindering chain segment twisting. Consequently, this enhances energy migration and energy transfer along the polymer network [22]. As a result, a broad spectrum spanning from blue to green or even yellow region is observed, which is not desirable for blue light emitting applications. In our case, however, this disadvantage is turned into an advantage for white light generation with azide group functionalization.

In this context, we intentionally used polyfluorene whose side chains can be substituted with a group facilitating the cross-linking. For example, bromide groups can be converted to azide groups to allow thermal or photochemical cross-linking [22-25]. Thus, it is known that by heating or UV-irradiation the azide group ($-N_3$) decomposes to a highly reactive nitrene ($-N:$) with the loss of nitrogen and the resulting nitrene can subsequently insert into side chains or the polymer backbone leading to the formation of cross-links, various nitrene species, and ring expansion [26,27]. This, in turn, causes a change in the polymer chain conformations and in optical properties of the polymer. With the intimate integration of the PFA thin film, the n-UV LED platform then serves as an efficient pump source for the excitation of PFA to generate a wide optical spectrum across the visible.

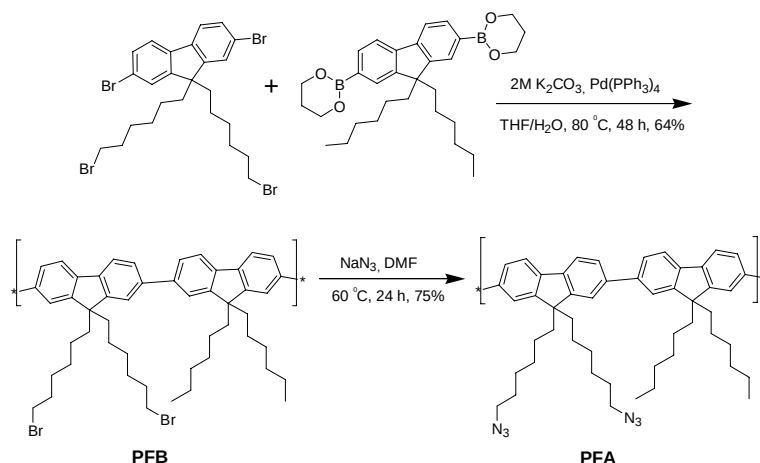


Fig. 2. Synthesis of poly[(9,9-dihexylfluorene)-*co-alt*-(9,9-bis-(6-bromohexyl)fluorene)] (PFB) and poly[(9,9-dihexylfluorene)-*co-alt*-(9,9-bis-(6-azidohexyl)fluorene)] (PFA).

For this purpose, first poly[(9,9-dihexylfluorene)-*co-alt*-(9,9-bis-(6-bromohexyl)fluorene)] (PFB) [21] was synthesized using Suzuki coupling conditions. Then the bromide groups were converted into azide groups by a nucleophilic substitution reaction using excess sodium azide in dimethylformamide (DMF) to obtain poly[(9,9-dihexylfluorene)-*co-alt*-(9,9-bis-(6-azidohexyl)fluorene)] (PFA) as yellow powder in moderate yield (Fig. 2). To synthesize PFB, 2,7-dibromo-9,9-bis-(6-bromo-hexyl)-9H-fluorene (975 mg, 1.5 mmol) and 9,9-dihexylfluorene-2,7-bis(trimethylborate) (754 mg, 1.5 mmol) were suspended in a mixture of degassed THF (15 ml) and H₂O (7 ml). Pd(PPh₃)₄ (21.0 mg) and K₂CO₃ (2.49 g, 18.0 mmol) were added sequentially. The mixture was degassed again and heated at 80 °C for 48 h under argon and then poured into methanol. The precipitate was collected by filtration and dissolved in chloroform. The solution was washed with water and concentrated under reduced pressure. The concentrated solution was poured into methanol; the solid residue was collected by centrifugation and dissolved in THF. The solution was added into stirred large excess of MeOH. The precipitate was finally collected by filtration and dried under vacuum to obtain yellowish powder of PFB [29]. To further synthesize PFA, PFB (300 mg, 0.36 mmol) and NaN₃ (60.0 mg, 1.08 mmol) were suspended in dry DMF (5 ml) and heated at 60 °C for 24 h. The mixture was poured into water (20 mL) and extracted with diethyl ether (50 mLx3). The combined organic layer was washed with water, dried over CaCl₂, and concentrated under reduced pressure. The residue was precipitated into methanol. The precipitate was collected by centrifugation and dried under vacuum to obtain yellow solid of PFA [30].

For the integrating platform, the InGaN/GaN based n-UV LED was epitaxially grown in a GaN dedicated metal organic chemical vapor deposition (MOCVD) reactor at Bilkent University Nanotechnology Research Center. After the growth of a nucleation layer, a GaN buffer layer was deposited, which was followed by the Si doped, GaN n-layer. Subsequently, 5 quantum wells and barriers with thickness of ~2 nm and ~3 nm, respectively, were grown as the active region to emit in the n-UV. A thin AlGaIn hole-blocking layer and finally a Mg doped p-layer were deposited on top of the active layer. The LED mesas were then fabricated using standard semiconductor fabrication procedure using reactive ion etch (RIE) and p- and n-types of ohmic contacts were metallized using thermal evaporation (metallization) and rapid thermal annealing, as also used in our previous work [31-35]. Figure 3 shows electroluminescence (EL) of the resulting n-UV LED with its EL peak at 378 nm and a full width at half maximum of 20 nm, along with its micrograph in the inset. Subsequently, for hybridization of the LED platform, PFA dissolved in THF at varying concentrations of 8-10 mg/mL was typically spun at 600 rpm for 10 seconds and 2000 rpm for 30 seconds, following

the cleaning and chemical treatment of its surface. The thickness of the resulting hybridized thin film was measured to be around 1.5 μm .

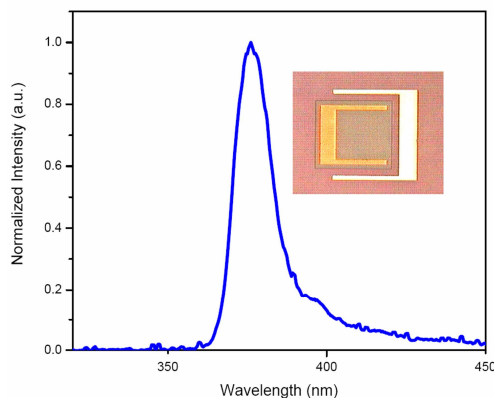


Fig. 3. Electroluminescence (EL) of our fully fabricated n-UV LED with its EL peak at 378 nm and a full width at half maximum of 20 nm, along with its micrograph in the inset.

3. Experimental demonstration of hybrid polyfluorene-based organic-inorganic WLEDs

Figure 4 shows the absorption and fluorescence spectra of the polymers in solution and in thin film, where the dashed-lines represent the polymers in solution and the solid-lines accordingly represent the polymers in solid state [for PFA in (a) and for the control group PFB in (b)]. An important characteristic of these polymers is that the fluorescence emission spectra are shifted sufficiently far from the absorption edge so that self-absorption is kept at a minimal level. This advantage is critical since this may have otherwise reduced the overall efficiency of our devices. The fluorescence quantum efficiencies of the PFA and PFB polymers in the solution of THF are recorded to be 0.86 and 0.88, respectively (with quinine sulfate used as the standard). The PL spectrum of the PFA thin film (shown in red curve), which spans from 420 nm to 650 nm, is significantly different than PFA in solution, whereas the PL spectrum of the thin film of the control group PFB is not as broad as the former spectrum and is not as much modified compared to PFB in solution. The origin of the observed highly broadened spectral emission of PFA in solid state across the visible range is attributed to the cross-linking azide functional group attached to the polymer backbone.

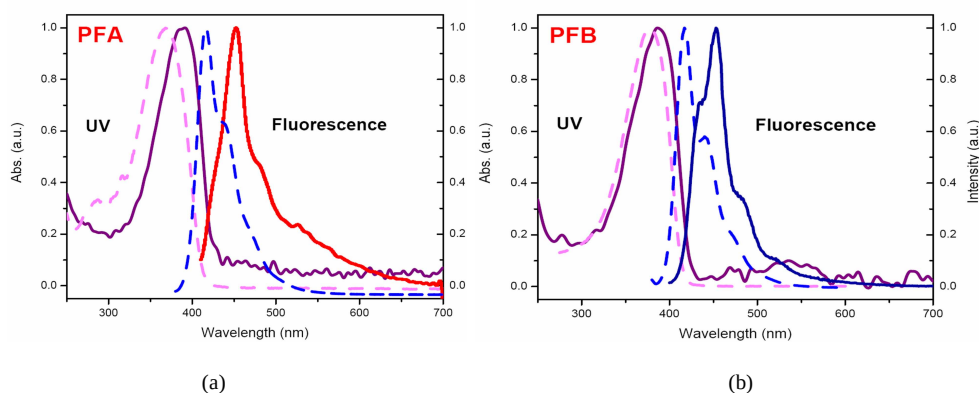


Fig. 4. (a). Absorption and fluorescence spectra of PFA and (b) PFB in tetrahydrofuran (THF) solution (dashed) and in film (solid).

In the solid state, the emission spectrum of the PFA film is observed to be very broad when integrated on the LED platform. Comparing the light coupled from the polymer hybridized LED and that from the uncoated LED in the integrating sphere, we observe that PFA emitters exhibit high light conversion efficiencies up to 70% in film. Using the experimentally measured values of the light conversion efficiency ($\eta_c=0.70$) and the absorbed pump light fraction ($f_\alpha=0.62$) in the conversion efficiency equation for a single-layer coated device [given in Eq. (1)], the solid-film PL quantum efficiency of PFA is calculated to be $\eta_{PL}=0.52$.

$$\eta_c = f_\alpha \eta_{PL} + (1 - f_\alpha) = 1 - f_\alpha (1 - \eta_{PL}) \quad (1)$$

In three device implementations of PFA-hybridized LEDs (Samples 1-3), using different LEDs and polymer solutions of various concentrations, we experimentally obtain the resulting tristimulus coordinates to be all in the white region of the C.I.E. chromaticity diagram (1931), with the coordinates of ($x=0.24$, $y=0.27$), ($x=0.29$, $y=0.28$), and ($x=0.26$, $y=0.24$), respectively. Figure 1 shows these (x , y) tristimulus coordinates on the C.I.E. chromaticity diagram (1931). These PFA-hybridized LEDs are measured to feature all very high color rendering indices of 86, 87, and 91, respectively. Here CRI represents the quality of the generated white light to reflect the true colors of objects when illuminated with these light sources. These CRIs are high again because of the desired broadening of the emission spectra of PFA due to intentional cross-linking in the film. Therefore, with all these CRIs reliably above 85, these PFA-hybridized LEDs provide high quality white light, meeting the CRI requirement of future solid-state based lighting >80.

Table 1. Chromaticity coordinates, color temperature, and color rendering index.

Samples		X	Y	T _c (K)	CRI
1	PFA	0.2434	0.2723	19634	86
2	PFA	0.2913	0.2770	9416	87
3	PFA	0.2554	0.2426	32371	91
Control (PFB)		0.1828	0.1477	34463	53

Table 1 summarizes (x , y) tristimulus coordinates and color rendering indices of Samples 1-3 (PFA hybridized LEDs) along with their corresponding correlated color temperatures. Additionally, Table 1 provides those of the control group, PFB-hybridized LED (Control), as the base-line performance. The control group exhibits a low color rendering index of 53 at most. Figure 5(a) shows the chromaticity coordinates of this control group with its optical emission in the inset when its integrating LED is electrically driven. With these tristimulus coordinates, the control group falls out of the white region due to lack of sufficient cross-linking. In contrary, Fig. 5(b) depicts the color coordinates and emission spectrum of the PFA-hybridized LED (Sample 3), with its quite broad photoemission when its integrating LED is electrically driven, leading to white light emission with high color rendering index of 91. As a result, the function of high-quality white light generation using a single-layer polyfluorene is activated with the azide group functionalization that facilitates cross-linking, significantly enhancing the resulting color rendering index by 72% (by 38 units) compared to the case of using the bromide functional group.

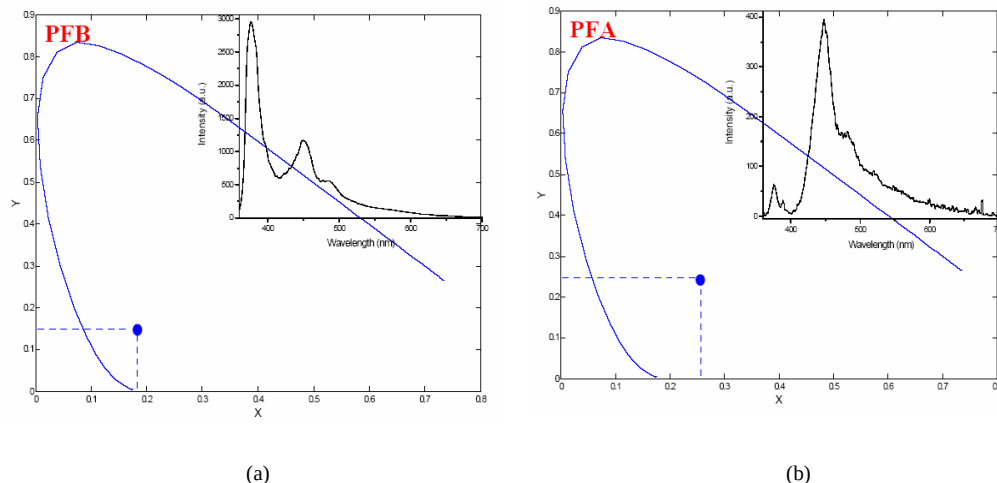


Fig. 5. Tristimulus color coordinates of (a) PFB-hybridized LED (Control) with CRI of 53 and (b) PFA-hybridized LED (Sample 3) with CRI of 91 respectively, along with their optical emission spectra in the inset when their respective integrating LEDs are electrically driven.

While the spectral broadening is not desired in polymers used for display applications, which are preferably aimed to operate at specific wavelengths, this is a desirable feature for white light generation applications. The ability of azide functionalized polyfluorene to feature the broadest spectrum across the visible caused by cross-linkable reacting species is specifically verified after an investigation of two sets of PFA, PFB and polyfluorene with no functional group (PF) samples after annealing one set of samples in air at various temperatures and the other set in argon at 220 °C for 2 h. In all three samples annealed in air the green emission band has a higher intensity than the blue emission band for annealing temperatures higher than 150 °C, as depicted in Fig. 6 for PFA only. On the other hand, the samples heated under argon exhibit different behavior as depicted in Fig. 7 for PF, PFB, and PFA.

In Fig. 6 the observed decrease in emission with increasing temperature occurs when the polymer is treated under such quite harsh conditions. Higher annealing temperatures cause the damages on the polymer chains. During the operation of the white LED, though, we also confirmed experimentally that the emitted power level of the device being driven at a current level of 30 mA at 4.5 V for 15 h, still exhibits the similar levels of light conversion efficiencies. Only very high annealing temperature (>150 °C) results in the degradation of polymer, which is not reached during the normal operation of WLED.

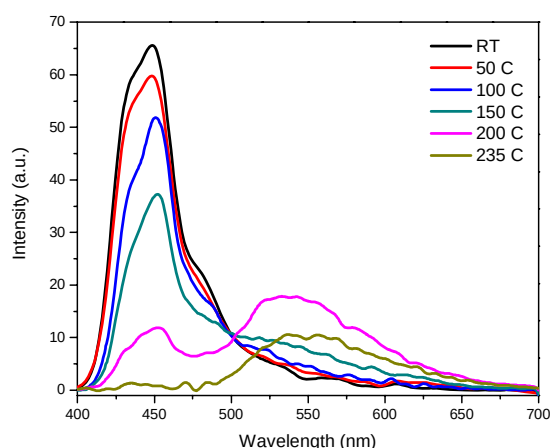


Fig. 6. Successive heat treatment of PFA thin film in air.

In Fig. 7(a), the blue emission dominates the spectrum of PF and it is similar to its pristine film. The spectrum of PFB shows an intense blue emission beside a green emission with low intensity in Fig. 7(b). On the other hand, while the intensity of the green emission band increases, the intensity of blue emission decreases in PFA shown in Fig. 7(c). This green emission band can occur not only because of keto defect formation, but it is considered to stem also from cross-linking [22, 25]. In the absence of oxygen, the polymers (PFB and PFA), which have cross-linkable groups, exhibited green emission; but not the one without any cross-linkable group (PF). One can see this effect in PFB at a lesser degree than PFA since azide is more labile than bromide and decompose to nitrene easily to form the cross-linked polymer. Thus, our experiments clearly indicate that even in the absence of oxygen the formation of green emission band is evident, which is attributed to cross-linking of azide, causing a broad spectrum formation spanning from blue to green-yellow. It seems that once excited species form, they can easily be transferred via intra-chain energy transfer because of the networked structure of the polymer.

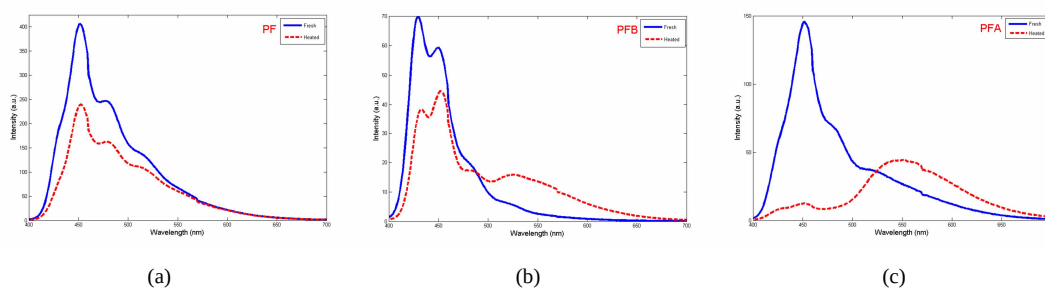


Fig. 7. Fluorescence spectra of (a) PF, (b) PFB, and (c) PFA when pristine (in blue) and after heat treatment at 220 °C for 2 h under argon (in red).

4. Conclusion

In conclusion, high-quality white light was generated by hybridizing a single layer of polyfluorene functionalized with azide on an n-UV LED with a maximum color rendering index of 91 and a light conversion efficiency of 70% at room temperature. A comparative study on the fluorescence emission from similar polyfluorene-type conducting polymers (PFA

and, as the control groups, PFB and PF) was also performed, demonstrating that the azide functionalization led to an enhancement factor of 72% (by 38 units) in CRI. This was due to the suppression of blue emission and the simultaneous broadening of the emission towards red in the PFA films. The cross-linking observed in the PFA film formation was considered to provide the key for the stability of PFA. Various heating experiments implied that the reaction intermediate nitrene possibly underwent an insertion to yield a network of polymer layer. The proof-of-concept demonstration of PFA-hybridized LEDs showed that the emission broadening of the PFA facilitated via the azide functional groups provides a rather cheap, simple, promising down-converting material for high-quality white light generation with high color rendering index and high light conversion efficiency.

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